

First-principles calculation of lattice thermal conductivities of α -, β -, and γ - Si_3N_4

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The lattice thermal conductivities of α -, β - and γ - Si_3N_4 phases are investigated from *ab-initio* anharmonic lattice dynamics, within the single-mode relaxation-time approximation of the linearized phonon Boltzmann transport equation. At 300 K, the lattice thermal conductivity of β - Si_3N_4 is calculated as $\kappa_{xx} = 73$ and $\kappa_{zz} = 199$ (in units of $\text{W m}^{-1} \text{K}^{-1}$), which is consistent with the reported experimental values of 69 and 180, respectively. For α - Si_3N_4 , $\kappa_{xx} = 68$ and $\kappa_{zz} = 100$ are obtained. The difference in anisotropy between these phases originates from the characteristic differences in their phonon band structures, which is closely related to the crystal structures. In α - Si_3N_4 , acoustic-mode phonons below 6 THz are the main heat carriers, while in β - Si_3N_4 , the phonon modes up to 12 THz contribute to the lattice thermal conductivity. In γ - Si_3N_4 , $\kappa = 77$ is obtained. The distribution of phonon mode contributions to the lattice thermal conductivity with respect to phonon frequency closely resembles that for κ_{xx} of β - Si_3N_4 , although the phonon lifetimes for γ - Si_3N_4 are twice as short as those for β - Si_3N_4 .

I. INTRODUCTION

Several nitride insulators are known to exhibit high thermal conductivity, which is important for heat transfer materials at elevated temperatures. For example, Slack *et al.*¹ reported that wurtzite-type AlN has thermal conductivity that exceeds $100 \text{ W m}^{-1} \text{K}^{-1}$. Si_3N_4 has become another promising thermal conductive insulator because its thermal conductivity has been improved up to $177 \text{ W m}^{-1} \text{K}^{-1}$ through the use of the advanced ceramic technologies related to densification and microstructure control.²⁻⁵ The Si_3N_4 ceramics also exhibit high mechanical strength at elevated temperatures; therefore, they are regarded as ideal materials for use in various applications, such as engine components, gas turbines, and heat sink substrates of power semiconductor devices.

At atmospheric pressure, Si_3N_4 has two phases, α and β , which are generally considered as low- and high-temperature phases, respectively.^{2,6,7} Their crystal structures belong to the $P31c$ and $P6_3/m$ space groups, respectively.^{8,9} These structures have different manners of stacking equivalent basal layer structures composed of SiN_4 tetrahedra.¹⁰ Fig. 1 depicts these layer structures from the principal axis direction. They are denoted as A, B, C, and D in the α phase, and A and B in the β phase. The stacking manners are thus ABCDABCD... and ABAB..., respectively. The α phase has additional two layer structures of C and D, which are related to A and B by the c glide operation.¹⁰ Along this direction, the lattice constant of the α phase is approximately twice as long as that of the β phase.

The experimental thermal conductivities^{2-5,12} of the Si_3N_4 polymorphs were measured for the bulk polycrystalline samples. These values were significantly affected by the lattice defects, impurities, shapes and orienta-

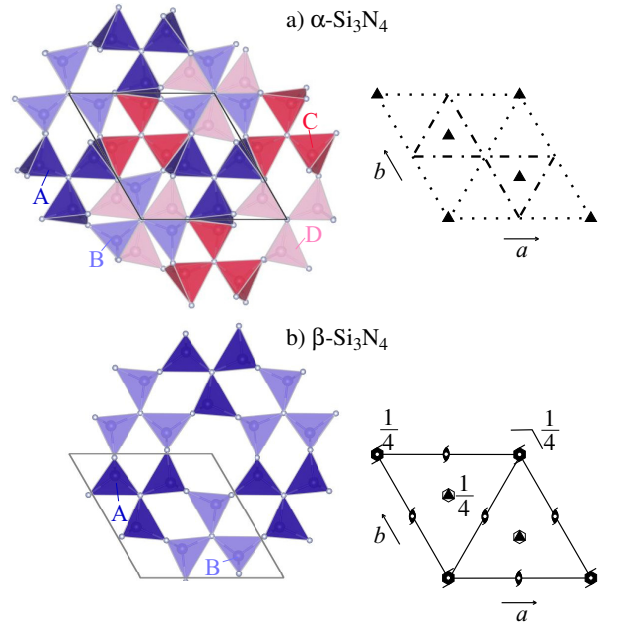


FIG. 1. (color online) Crystal structures of α - and β - Si_3N_4 . Stacking of SiN_4 tetrahedron layers are shown at the left. (a) ABCDABCD... for α - Si_3N_4 . (b) ABAB... for β - Si_3N_4 . Space group diagrams¹¹ for $P31c$ (α - Si_3N_4) and $P6_3/m$ (β - Si_3N_4) are shown at the right.

tions of the constituent crystal grains;⁶ the intrinsic thermal conductivity of defect-free Si_3N_4 has not been established. As an experimental approach to determine this, Li *et al.*¹³ applied the high-resolution thermoreflectance microscopy to single β - Si_3N_4 grains in a ceramic sample. The thermal conductivity was analyzed as 69 and $180 \text{ W m}^{-1} \text{K}^{-1}$ along the a and c axes, respectively. These val-

ues respectively correspond to the xx and zz elements of the lattice thermal conductivity tensor, κ . We consider the anisotropy of $\kappa_{zz}/\kappa_{xx} \sim 3$ is relatively large. Hirotsaki *et al.*⁶ theoretically estimated κ by application of the Green-Kubo formulation to the molecular dynamics (MD) method with the interatomic potentials proposed by Vashishta *et al.*¹⁴. They calculated κ_{xx} and κ_{zz} of α -Si₃N₄ to be 105 and 225 W m⁻¹ K⁻¹, and those of β -Si₃N₄ as 170 and 450 W m⁻¹ K⁻¹, respectively. The ratio κ_{zz}/κ_{xx} in β -Si₃N₄ agreed well with the experimental ratio; κ_{xx} and κ_{zz} were overestimated by more than two times **that** of the experimental κ .

Based on first principles calculations and Boltzmann transport theory¹⁵, Togo *et al.* recently calculated κ of many polymorphs of the zincblende- and wurtzite-type structures. Their crystal structures have stacking manners of the densest atom planes as ABCABC... and ABAB..., respectively. The different stacking manners merely altered κ , the phonon linewidths and the phonon density of states (DOS).¹⁵ On the other hand, the previous MD results indicated that the different stacking manners between the α and β phases altered κ significantly. This has not been explained with respect to their phonon properties. Therefore, it is of interest to investigate this based on the first principles anharmonic phonon calculation.

In addition to the α and β phases, a cubic spinel phase (γ -Si₃N₄) is known to form upon compression and *in situ* heating.^{16,17} The reported transition pressures are scattered from 10 to 36 GPa, depending on the experimental conditions.¹⁸ The γ phase is experimentally quenched to atmospheric pressure and room temperature. The thermal conductivity of the γ phase has not been experimentally reported, although it has been estimated by the Slack model.¹⁹

The present study aims to qualitatively elucidate the lattice thermal conductivity tensors among the three Si₃N₄ phases by a first principles approach. We calculate κ of the γ phase as well, for systematic understanding. After the methodology section, we examine the validity of the present results. The calculated thermal properties are then compared with the available experimental and theoretical references. The characteristic behaviors of κ are then investigated in detail on the basis of the phonon band structures and phonon linewidths.

II. COMPUTATIONAL PROCEDURES

A. Lattice thermal conductivity calculation

The lattice thermal conductivities were calculated by solving the linearized Boltzmann transport equation (LBTE) within the single-mode relaxation time approximation (single-mode RTA). The harmonic phonon states and lattice thermal conductivities were calculated with the phonopy²⁰ and phono3py¹⁵ software packages, respectively. We also attempted the direct-solution of

LBTE²¹ and give the calculated κ values in the following section. The **difference** between κ calculated by the single-mode RTA and that by the direct solution was to be minor for our discussion. Therefore, this research was limited to use the single-mode RTA to take advantage of its **intuitive** closed form of κ .

In the following sections, we denote the phonon mode by $\lambda = (\mathbf{q}, p)$ with the set of the phonon wave vector \mathbf{q} and band index p and $-\lambda \equiv (-\mathbf{q}, p)$. The relaxation time due to phonon-phonon scattering was obtained as half the reciprocal of linewidth, $\tau_{\lambda, \text{ph-ph}} = (2\Gamma_{\lambda})^{-1}$, where the linewidth that was employed is as follows:

$$\Gamma_{\lambda} = \frac{18\pi}{\hbar^2} \sum_{\lambda'\lambda''} |\Phi_{-\lambda\lambda'\lambda''}|^2 \times \{ (n_{\lambda'} + n_{\lambda''} + 1) \delta(\omega_{\lambda} - \omega_{\lambda'} - \omega_{\lambda''}) + (n_{\lambda'} - n_{\lambda''}) [\delta(\omega_{\lambda} + \omega_{\lambda'} - \omega_{\lambda''}) - \delta(\omega_{\lambda} - \omega_{\lambda'} + \omega_{\lambda''})] \}. \quad (1)$$

Here, ω_{λ} is the harmonic phonon frequency of the phonon mode λ , $n_{\lambda} = [\exp(\hbar\omega_{\lambda}/k_{\text{B}}T) - 1]^{-1}$ is the Bose-Einstein distribution at temperature T , and $\Phi_{\lambda\lambda'\lambda''}$ denotes the three-phonon-scattering strength. $\Phi_{\lambda\lambda'\lambda''}$ was obtained by the usual coordinate transformation of third-order force constants from direct space to phonon space.¹⁵ The second- and third-order real-space force constants were obtained by *ab initio* calculation, of which the details are given in the next section.

To more realistically compare the calculated κ with the measured thermal conductivities, the isotopic scattering effect due to the natural isotope distribution was taken into account according to the second-order perturbation theory.²² Using the relaxation times for the phonon-phonon scattering and isotopic scattering, $\tau_{\lambda, \text{ph-ph}}$ and $\tau_{\lambda, \text{iso}}$, respectively, the total relaxation time for a phonon mode, τ_{λ} , was calculated by assuming Matthiessen's rule, $1/\tau_{\lambda} = 1/\tau_{\lambda, \text{ph-ph}} + 1/\tau_{\lambda, \text{iso}}$.

The experimental thermal conductivities in the Si₃N₄ system were measured for the polycrystalline samples and not from single crystals. The conductivities measured in a polycrystalline area were affected by various lattice defects within that area, such as grain boundaries, impurities, and vacancies. We crudely took them into account by the relaxation time $\tau_{\lambda, \text{bs}} = L/|\mathbf{v}_{\lambda}|$ of a phonon boundary scattering model, where $\mathbf{v}_{\lambda} = \nabla_{\mathbf{q}}\omega_{\lambda}$ is the group velocity and L is a parameter related to the boundary mean free path. We consider $\tau_{\lambda, \text{bs}}$ as a variable parameter and partly include it in the calculated κ , according to Matthiessen's rule.

The closed form of κ within the RTA was obtained via

$$\kappa(T) = \frac{1}{N_{\mathbf{q}}\Omega} \sum_{\lambda} \tau_{\lambda}(T) \mathbf{v}_{\lambda} \otimes \mathbf{v}_{\lambda} c_{\lambda}(T), \quad (2)$$

where $N_{\mathbf{q}}$ is the number of \mathbf{q} -points, Ω is the unit cell volume, and c_{λ} is the mode heat capacity. To analyze κ

in detail, the cumulative thermal conductivity:

$$\kappa^c(\omega) = \frac{1}{N_{\mathbf{q}}\Omega} \int_0^\omega \sum_{\lambda} \tau_{\lambda}(T) \mathbf{v}_{\lambda} \otimes \mathbf{v}_{\lambda} c_{\lambda}(T) \delta(\omega' - \omega) d\omega', \quad (3)$$

and its derivative $\frac{\partial \kappa^c(\omega)}{\partial \omega}$, were calculated to determine the phonon mode contributions to κ .

B. Computational details

The force constants required for the lattice dynamics were calculated using the first-principles projector augmented wave method²³ (VASP code^{24–26}). The generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof²⁷ was used for the exchange correlation potential. A plane wave energy cutoff of 500 eV was employed. The crystal structures were optimized for 0 K and 0 GPa until the residual forces acting on the constituent atoms were less than 10^{-6} eV Å⁻¹. Here, the temperature and pressure were considered only for the electronic system and the zero point lattice vibration was not considered. The calculated lattice parameters were $a = 7.808$ Å and $c = 5.659$ Å for the α phase, $a = 7.660$ Å and $c = 2.925$ Å for the β phase, and $a = 7.787$ Å for the γ phase, which are in agreement with the experimental data^{8,9,28} within +0.7 % error. The lattice volume optimized with the local density approximation (LDA)²⁹ for the exchange correlation potential was, for β -Si₃N₄, 3 % smaller than the volume optimized with GGA, which is a typical volume contraction of LDA. κ_{xx} and κ_{zz} calculated with LDA were larger by 0.3 and 2.6 % than those calculated with GGA. For our discussion, these differences are sufficiently small; therefore, the impact of the choice of exchange correlation potential is considered to be minor in this study.

The force constants were calculated by the finite difference approach³⁰. For this calculation, the following supercells were adopted: $1 \times 1 \times 2$, $1 \times 1 \times 3$, and $1 \times 1 \times 1$ supercells of the conventional unit cells for the calculations of the third-order force constants of α , β , and γ -Si₃N₄, respectively, and $3 \times 3 \times 4$, $3 \times 3 \times 8$ and $2 \times 2 \times 2$ for those of the second-order force constants. The length of the induced atomic displacements was set to 0.03 Å. Table I shows κ calculated with several different sets of the supercells, which indicates that the calculated κ has reasonable convergence with respect to the size of the supercells.

Uniform \mathbf{k} -point sampling meshes of $4 \times 4 \times 2$, $4 \times 4 \times 3$, and $3 \times 3 \times 3$ were employed for calculations of the third-order force constants of the α , β , and γ phases. For the α and β phases, the center of the a^*b^* plane was sampled, while the center on the c^* -axis was not. For the γ phase, a non- Γ center mesh was used. For the calculations of the second-order force constants, the Γ -point was only sampled for the α and β phases, and the only one $\mathbf{k} = (0.5, 0.5, 0.5)$ point was sampled for the γ

TABLE I. Calculated lattice thermal conductivities of α -, β -, and γ -Si₃N₄ (WK⁻¹m⁻¹) at 300 K with respect to several combinations of supercell sizes.

| Phase | Supercell (# of atoms) | | LTC | |
|----------|---------------------------------|---------------------------------|------|------|
| | 3 rd force constants | 2 nd force constants | xx | zz |
| α | $1 \times 1 \times 1$ (28) | $1 \times 1 \times 1$ (28) | 37 | 57 |
| | $1 \times 1 \times 2$ (56) | $1 \times 1 \times 2$ (56) | 41 | 79 |
| | $1 \times 1 \times 1$ (28) | $2 \times 2 \times 2$ (224) | 55 | 81 |
| | $1 \times 1 \times 2$ (56) | $2 \times 2 \times 2$ (224) | 67 | 95 |
| | $1 \times 1 \times 2$ (56) | $2 \times 2 \times 3$ (336) | 68 | 97 |
| | $1 \times 1 \times 2$ (56) | $3 \times 3 \times 4$ (1008) | 68 | 100 |
| β | $1 \times 1 \times 2$ (28) | $1 \times 1 \times 2$ (28) | 44 | 173 |
| | $1 \times 1 \times 2$ (28) | $2 \times 2 \times 4$ (224) | 76 | 208 |
| | $1 \times 1 \times 3$ (42) | $2 \times 2 \times 4$ (224) | 71 | 194 |
| | $1 \times 1 \times 3$ (42) | $2 \times 2 \times 5$ (280) | 72 | 196 |
| | $1 \times 1 \times 3$ (42) | $3 \times 3 \times 8$ (1008) | 73 | 199 |
| γ | $1 \times 1 \times 1$ (56) | $1 \times 1 \times 1$ (56) | 72 | |
| | $1 \times 1 \times 1$ (56) | $2 \times 2 \times 2$ (448) | 77 | |
| | $1 \times 1 \times 1$ (56) | $3 \times 3 \times 3$ (56) | 79 | |

phase. The \mathbf{q} -point sampling meshes of $10 \times 10 \times 14$, $10 \times 10 \times 26$, and $12 \times 12 \times 12$ were employed to calculate κ in Eq. (2) for the α , β , and γ phases, respectively.

Non-analytical term correction³¹ was applied to the second-order force constants to take into account the long range coulombic forces present in ionic crystals. For the correction, static dielectric constants and Born effective charges were calculated using the density functional perturbation theory as implemented in the VASP code^{32,33}.

The effect of lattice thermal expansion on κ was examined by the calculation of κ for several finite temperatures with the crystal structures optimized for the corresponding temperatures within the quasi-harmonic approximation (QHA)³⁴. These κ were different from those calculated for the same temperatures with the structure optimized for 0 K. We consider these differences as the effect of lattice thermal expansion. **The differences in κ for $T=300, 600, 900, 1200$, and, 1500 K, for the β phase, were within 1 %. The magnitude was similar to that for Si and Ge calculated by Ward *et al.*³⁵.** For the present study, these differences are negligible and for finite temperatures κ calculated with the structure optimized for 0 K was adopted.

The volumetric thermal expansion coefficients were also calculated. **Comparison with the experimental coefficient is useful to validate the present thermal conductivity calculation because both the thermal expansion and κ originate from the anharmonicity of the interatomic potential.** The calculated coefficients of the α , β , and γ phases were 4.31×10^{-6} , 4.19×10^{-6} , and 1.13×10^{-5} K⁻¹ for 300 K, while the experimental values^{36,37} were 3.75×10^{-6} , 3.55×10^{-6} , and 9.48×10^{-6} K⁻¹. The calculation systematically overestimated the experimental values, but reproduced the experimental tendencies, in-

cluding that the α phase has a slightly larger thermal expansion coefficient than the β phase. This supports the validity of the present calculation to qualitatively compare the calculated κ among the Si_3N_4 phases.

To compare the microscopic phonon properties among the three phases under the same conditions, the results calculated at 0 GPa are shown and discussed. For the γ phase, this means that we assume the condition of a virtually quenched γ phase at 0 GPa from the high pressure. To examine the analytical continuity of the properties with respect to pressure, κ of the γ phase was calculated at 10, 20, and 40 GPa, as shown in Fig. 9. The phenomenological behavior of the linear dependence of κ with respect to the pressure was reproduced, similar to that in Ref. 38. The slope was $2.89 \text{ W m}^{-1} \text{ K}^{-1} \text{ GPa}^{-1}$ for the γ phase. From this dependence, we consider that the microscopic values are also varied smoothly with the pressure and those at 0 GPa are valuable for comparison with the corresponding values of the α and β phases.

C. Direct solution of LBTE

The advantage of employing the single-mode RTA for thermal conductivity calculations is the closed form, by which the qualitative character of κ can be intuitively understood in terms of the phonon-mode specific properties. The microscopic understanding of the full solution of LBTE is still under development,³⁹ and the microscopic picture based on collective phonons⁴⁰ will require more complicated investigation.

Single-mode RTA solutions of LBTE often underestimate the full solution.^{35,41} To check this underestimation, κ for the α and β phases were calculated by the direct solution of LBTE²¹, which is one of the methods of LBTE full solutions. κ_{xx} and κ_{zz} without the isotope effect were 69 and $102 \text{ W m}^{-1} \text{ K}^{-1}$ for the α phase, and 76 and $238 \text{ W m}^{-1} \text{ K}^{-1}$ for the β phase, respectively, while the corresponding single-mode RTA values were 70 and $102 \text{ W m}^{-1} \text{ K}^{-1}$ for the α phase, and 76 and $210 \text{ W m}^{-1} \text{ K}^{-1}$ for the β phase. κ_{zz} for the β phase from the direct solution was 13 % larger than that of the single-mode RTA solution. The differences in κ between the LBTE solutions are not significant; therefore, we expect that the physics of these lattice thermal conductivities can be well understood within the single-mode RTA at the current level of our interest. Therefore, we discuss the lattice thermal conductivities calculated by the single-mode RTA solution.

III. RESULTS AND DISCUSSION

A. Lattice thermal conductivities

Table II shows the calculated κ for 300 K. $\beta\text{-Si}_3\text{N}_4$ has a markedly more anisotropic κ than $\alpha\text{-Si}_3\text{N}_4$. The directional averages $\sum_i \kappa_{ii}/3$ are 79, 115, and 77 W m^{-1}

TABLE II. Calculated thermal conductivities of $\alpha\text{-Si}_3\text{N}_4$ (trigonal), $\beta\text{-Si}_3\text{N}_4$ (trigonal), and $\gamma\text{-Si}_3\text{N}_4$ (cubic) at 300 K in units of $\text{W m}^{-1} \text{ K}^{-1}$, compared with the experimental and theoretical reference data. Theoretical bulk moduli B (in units of GPa), calculated using the present band method are presented in the fourth column.

| | This work | | | κ | Ref. Theo. | | Ref. Expt. | |
|--------------------------------|---------------|---------------|-----|------------------|------------------|------------------|-----------------|------------------|
| | κ_{xx} | κ_{zz} | B | | κ_{xx} | κ_{zz} | κ_{xx} | κ_{zz} |
| $\alpha\text{-Si}_3\text{N}_4$ | 68 | 100 | 224 | 70 ^a | 105 ^b | 225 ^b | - | - |
| $\beta\text{-Si}_3\text{N}_4$ | 73 | 199 | 237 | 250 ^a | 170 ^b | 450 ^b | 69 ^c | 180 ^c |
| $\gamma\text{-Si}_3\text{N}_4$ | 77 | - | 296 | 80 ^a | - | - | - | - |

^a Ref. 19, Slack model.

^b Ref. 6, molecular dynamics (Green-Kubo).

^c Ref. 13, single crystalline grains of polycrystals.

K^{-1} for the α , β , and γ phases, respectively. The value for the γ phase is similar to that for the α phase, despite the comparatively large difference among the bulk moduli (B) that are also shown in Table II.

Table II also lists the previously reported experimental¹³ and theoretical⁶ κ for references. The theoretical results¹⁹ of the Slack model, which do not include the anisotropy in κ , are shown as κ in Table II. Compared to the κ from MD⁶, our κ for the β phase has better agreement with the experimental κ . Compared to κ from the Slack model, our directional average $\sum_i \kappa_{ii}/3$ is also much closer to the experimental average.

Fig. 2 shows the theoretical κ for the α and β phases as a function of T , together with the reference experimental data^{5,12}. The experimental thermal conductivities for a series of temperatures were measured on polycrystalline areas by the laser flash method. These thermal conductivities (denoted as $\kappa_{\text{polycrystal}}$) cannot be directly compared with the calculated intrinsic κ , because they are largely dependent on the microstructure of the samples; they deviate from the simple directional averages of the intrinsic κ_{ii} , depending on the shapes of the crystal grains. We treated this effect using the parameter $0 \leq w \leq 1$ and fitting the quantity $w\kappa_{xx} + (1-w)\kappa_{zz}$ to the experimental $\kappa_{\text{polycrystal}}$ by the least squares method. We regard this as theoretical $\kappa_{\text{polycrystal}}$.

In Fig. 2, κ_{ii} calculated without $\tau_{\lambda, \text{bs}}$ are almost proportional to T^{-1} because n_λ in Eq. (1) can be reduced to $\frac{k_B T}{\hbar \omega_\lambda} - \frac{1}{2}$. In Fig. 2(a), the experimental $\kappa_{\text{polycrystal}}$ of a chemically vapor-deposited $\alpha\text{-Si}_3\text{N}_4$ sample¹² is not proportional to T^{-1} and intersects the theoretical κ_{ii} . Thus, w does not adjust the theoretical $\kappa_{\text{polycrystal}}$ to the experimental $\kappa_{\text{polycrystal}}$. The full solution of LBTE would negligibly cure the disagreement. Including the simple phonon lifetime of boundary scattering, $\tau_{\lambda, \text{bs}} = L/|\mathbf{v}_\lambda|$, into the total phonon lifetime could not explain the discrepancy either. A L value of $0.6 \mu\text{m}$, which was much smaller than the experimental grain size¹² of $10 \mu\text{m}$, decreased the theoretical κ_{ii} at the low temperature side toward the experimental values; however, κ_{ii} at the high

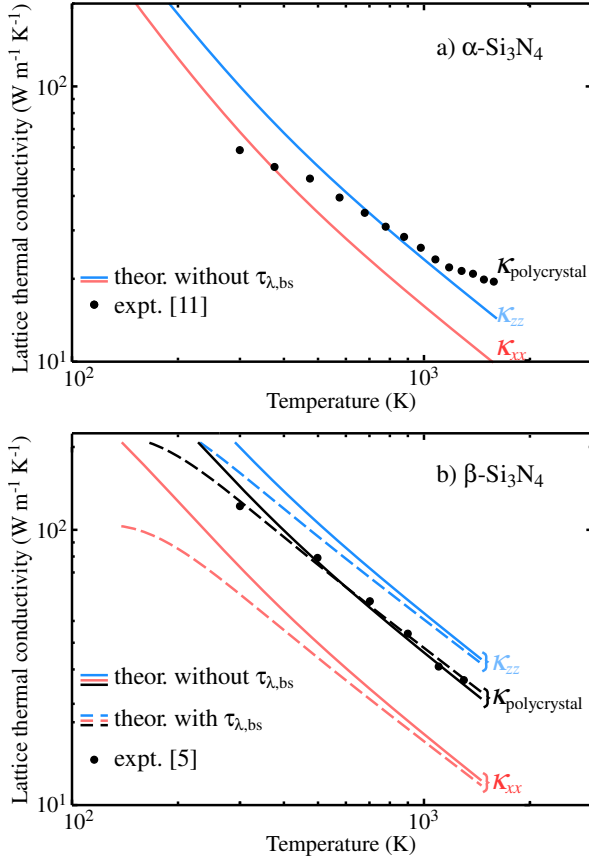


FIG. 2. (color online) Dependence of thermal conductivity on the temperature for α - and β - Si_3N_4 . For β - Si_3N_4 , theoretical conductivities with the boundary scattering effect are shown by broken lines. Theoretical $\kappa_{\text{polycrystal}}$ (see text) for the β - Si_3N_4 sample are also shown for comparison with the experimental conductivities.

temperature side continued to be significantly smaller than the experimental values. At present, the reason for the discrepancy between the theoretical and experimental behavior is unclear. Although the crystal structure of the experimental sample was characterized as α - Si_3N_4 , significant lattice defects were present in the sample, as pointed out by Hirotsaki *et al.*⁶, so that the simple phonon boundary scattering model may fail to describe their effects on the $\kappa_{\text{polycrystal}}$.

For the β phase, the experimental $\kappa_{\text{polycrystal}}$ is located in-between the theoretical κ_{xx} and κ_{zz} curves, being almost proportional to T^{-1} . Simple directional averages of the theoretical κ_{ii} slightly underestimate these experimental values. This is understood from the control of the microstructure to increase $\kappa_{\text{polycrystal}}$, and the crystalline grains were selectively grown along the c axis of the most conductive direction.⁵ The theoretical $\kappa_{\text{polycrystal}}$ was fit well with $w = 0.44$ to the experimental. For the effects of lattice defects most of which were grain boundaries, $\tau_{\lambda,bs}$ was included with $L = 0.6 \mu\text{m}$ to further fit the theoretical curve ($w = 0.33$) to the experimental data. L

is slightly smaller than the average grain size⁵ of $2 \mu\text{m}$ in the experiment; therefore, the discrepancy can presumably be explained by the presence of other lattice defects than by the grain boundaries.

B. Dispersion curves

Fig. 3 shows phonon band diagrams for the three Si_3N_4 phases. The branches are classified according to their symmetry groups, using different colors and line styles. The solid and dashed lines are used to represent degenerate and non-degenerate modes, respectively. The band diagrams on the other high-symmetry paths are almost identical to those reported earlier^{18,42} and thus are not shown. Here we investigate the frequency gradients, the group velocities projected on the paths, with particular focus on their anisotropy in the α and β phases. This was not investigated in the previous works.

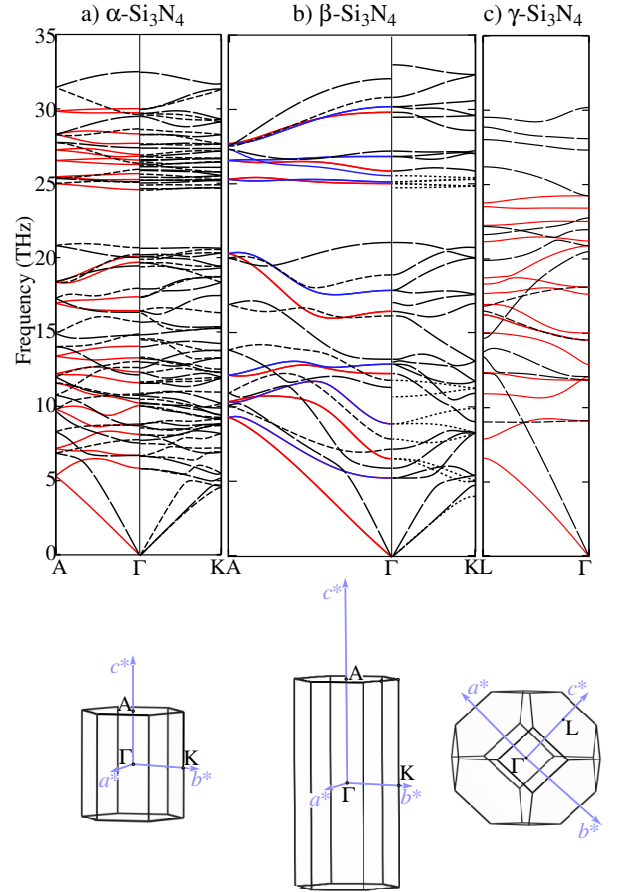


FIG. 3. (color online) Calculated phonon band diagrams (top) for three Si_3N_4 phases and Brillouin-zones (bottom).

The α phase unit cell contains two times more basal layer structures than the β phase unit cell; therefore, the edge of the α phase Brillouin zone in stacking direction A is half as far as that of the β phase. The number of

phonon branches in the α phase are twice that in the β phase. Phonon branches that are adjacent in frequency and belong to the same symmetry group generally show a band gap, and an anticrossing occurs when they are close to each other. If we regard the α phase lattice as a superlattice of the β phase lattice, then the phonon branches of the α phase in Fig. 3(a) are produced by folding the phonon branches of the β phase at the perpendicular bisector plane of ΓA . Taking for example the folding of the acoustic phonon branch, in Fig. 3(a), an upper branch that belongs to the same symmetry group is located very close in frequency, which inevitably entails an anticrossing and a band gap between them. This explains why the folded branch, which is degenerate at A with the acoustic branch due to the non-symmorphic symmetry, can not increase its frequency as it goes back on ΓA in Fig. 3(a). The band gap and anticrossings are reported in the theoretical study on the lattice thermal conductivities of GaAs/AlAs superlattices.⁴³ It is interesting that these effects occur in the present system, due to the stacking manners of the unit structures composed of the same elements.

As a result, in Fig. 3(a), the acoustic phonon branches increase their frequencies similarly between these paths. In contrast, the corresponding frequencies in Fig. 3(b) increase much more from Γ to A than from Γ to K. The anisotropic frequency increments indicate an anisotropic \mathbf{v}_λ . Compared with the α and γ phases, the β phase shows significantly steep slopes for the low frequency optical phonon branches on ΓA , which indicates that $v_{\lambda,z}$ of these phonon modes are large. The anisotropic \mathbf{v}_λ of the acoustic and low-frequency optical phonons will be investigated further in the following sections.

In the γ phase, the longitudinal acoustic branches maintain linear dispersion at higher frequencies than in the other phases. The gradients of ω_λ for the γ phase are the largest among the three phases, as expected by the largest B .

C. ω_λ contour map on the reciprocal plane

We investigate the anisotropy in \mathbf{v}_λ of α - and β - Si_3N_4 phases using another geometry, i.e., a cross-section of the Brillouin-zone. Fig. 4 shows contour maps of ω_λ on the b^*c^* plane. We show the maps for the four lowest-frequency bands because they contribute significantly to κ , which will be confirmed in the next section. There were negligible differences between the distributions on the b^*c^* plane and the other planes containing the c^* axis. Therefore, the b^*c^* plane was selected as a representative plane. In the α phase, the ω_λ distributions and thus \mathbf{v}_λ are almost isotropic. In the β phase, the contours are rather parallel to the b^* axis, and thus the \mathbf{v}_λ tends to orient toward the c^* axis direction. This confirms the large anisotropy of \mathbf{v}_λ of the acoustic and low-frequency optical phonon branches for the β phase.

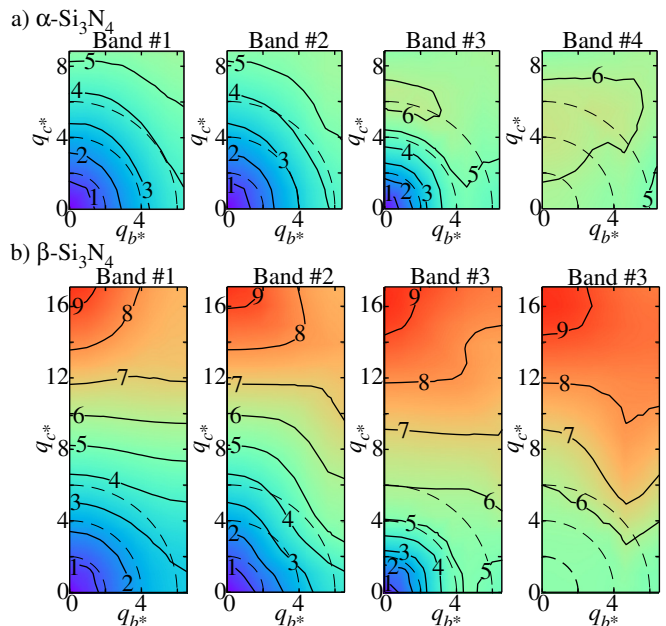


FIG. 4. (color online) Contour maps of phonon frequency (THz) on the b^*c^* planes of Brillouin-zones. The coordinates in the reciprocal plane are in units of 10^{-2} \AA^{-1} . The maps for the four lowest-frequency phonon modes are shown. The frequency landscapes are formed by simply connecting the frequencies of the same band indices, assigned in ascending order of frequency at the respective \mathbf{q} points.

D. Frequency distributions of phonon properties

In the previous two sections, we have investigated the anisotropy in \mathbf{v}_λ , which may explain the anisotropy in κ . Here we examine which phonon frequencies and which terms in the RTA closed form characterize the behavior of the present κ . In the following, we disregard the term of mode heat capacity because it is approximately constant for 300 K. For simplicity, the effects of isotope scattering and boundary scattering are not considered. For the investigation, the cumulative thermal conductivity, $\mathbf{k}^c(\omega)$ in Eq.(3), and its derivative $d\mathbf{k}^c/d\omega$, are shown at the top of Fig. 5. From this figure, it is evident that in the α , β , and γ phases, the phonon modes with their frequencies up to ca. 6, 12 and 10 THz largely contribute to each respective κ . The frequencies shown in the contour maps in Fig. 4 are within these frequency ranges, and thus it is confirmed that these bands make a significant contribution to κ .

Assuming that τ_λ and \mathbf{v}_λ are constant, then $d\kappa_{ii}^c/d\omega$ ($ii=xx, zz$) are proportional to the phonon DOS:

$$g(\omega) = \frac{1}{N_{\mathbf{q}}\Omega} \sum_{\lambda} \delta(\omega - \omega_{\lambda}). \quad (4)$$

In this context, we view $g(\omega)$ as frequency distributions of heat carrier density. Alternatively, assuming that only

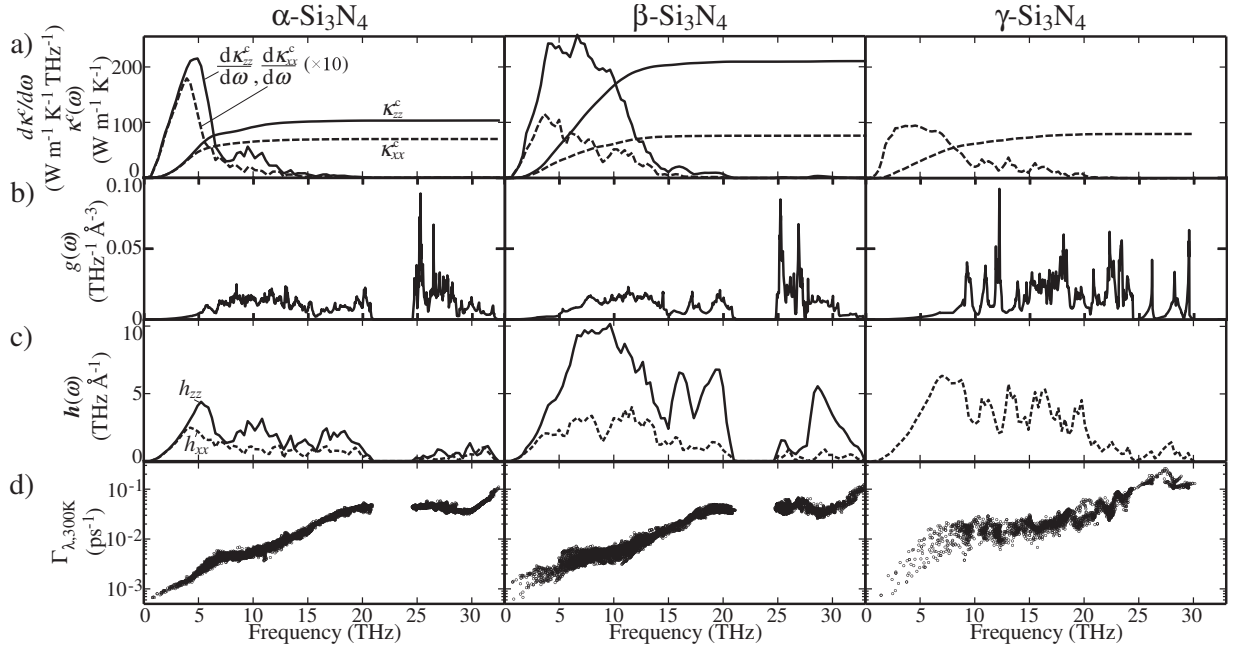


FIG. 5. (color online) Microscopic phonon properties of three Si_3N_4 phases. (a) Cumulative thermal conductivity κ^c and its frequency derivative, (b) DOS as $g(\omega)$, (c) DOS weighted with $\mathbf{v}_\lambda \otimes \mathbf{v}_\lambda$ as $\mathbf{h}(\omega)$, and (d) scatter plots of linewidths and phonon frequencies, $(\Gamma_\lambda, \omega_\lambda)$.

τ_λ is constant, then $d\kappa^c/d\omega$ is proportional to:

$$\mathbf{h}(\omega) = \frac{1}{N_{\mathbf{q}}\Omega} \sum_{\lambda} \mathbf{v}_\lambda \otimes \mathbf{v}_\lambda \delta(\omega - \omega_\lambda), \quad (5)$$

from which we examine the impacts of both of \mathbf{v}_λ and the heat carrier density. $g(\omega)$ and $\mathbf{h}(\omega)$ are shown in Figs. 5(b) and (c). As for the frequency variation of $\tau_{\lambda, ph-ph}$, the phonon linewidths are shown as scatter plots of $(\Gamma_\lambda, \omega_\lambda)$ in Fig. 5(d).

Comparing between the α and β phases, their linewidth distributions are qualitatively similar, except for a striking difference below ~ 5 THz, which will be examined later. The markedly different $d\kappa_{ii}^c/d\omega$ between the two phases are therefore ascribed to the corresponding h_{ii} . Moreover, because the overall spectral shapes of $g(\omega)$ are also similar between the two phases, the \mathbf{v}_λ alone accounts for the different behaviors of the $d\kappa_{ii}^c/d\omega$. Thus we conclude that the different anisotropy in κ is qualitatively explained by the different \mathbf{v}_λ , due to the folding effects of the band gaps and anticrossings. In contrast to this, in the case of the zincblende and wurtzite structures, the group velocities are suggested to be similar from their band structures¹⁵, because the anticrossings are not created by the folding, as the optical branches are located at much higher frequencies than in the present system. This must result in the similar κ between these structures, irrespective of the stacking manners.

The γ phase has much different $g(\omega)$, $\mathbf{h}(\omega)$, and, Γ_λ from the others as expected from the large differences in the crystal structure. The most significant difference is in

its phonon linewidths. Below ~ 10 THz, they are approximately twice larger than those of the other phases. We will examine this details later. As a result, the $d\kappa_{xx}^c/d\omega$ shows relatively low intensities. Since the longitudinal acoustic phonon branch increases its frequencies much, as we have examined in the band diagram, $d\kappa_{xx}^c/d\omega$ rather gradually attenuates as frequency increases, occasionally resembling to $d\kappa_{xx}^c/d\omega$ of the β phase.

It is left curious that the linewidths are similar between the α and β phases although the group velocities show marked differences between them. In analogy to Lindsay *et al.*⁴⁴, we can say that Γ_λ in the present form depends on the phase space for the available two phonons, $\{\lambda', \lambda''\}$, and also depends on $|\Phi_{\lambda\lambda'\lambda''}|^2$. We examine these terms one-by-one. A distribution of two-phonon configurations is represented as a joint density of states (JDOS), $D_2(\mathbf{q}, \omega)$,

$$D_2(\mathbf{q}, \omega) = D_2^{(1)}(\mathbf{q}, \omega) + D_2^{(2)}(\mathbf{q}, \omega) \quad (6)$$

where

$$\begin{aligned} D_2^{(1)} &= \frac{1}{N_{\mathbf{q}}Z^2} \sum_{\lambda'\lambda''} \Delta(-\mathbf{q} + \mathbf{q}' + \mathbf{q}'') \\ &\times [\delta(\omega + \omega_{\lambda'} - \omega_{\lambda''}) + \delta(\omega - \omega_{\lambda'} + \omega_{\lambda''})], \\ D_2^{(2)} &= \frac{1}{N_{\mathbf{q}}Z^2} \sum_{\lambda'\lambda''} \Delta(-\mathbf{q} + \mathbf{q}' + \mathbf{q}'') \\ &\times \delta(\omega - \omega_{\lambda'} - \omega_{\lambda''}), \end{aligned}$$

with $\Delta(\mathbf{x})$ giving 1 if \mathbf{x} is a reciprocal lattice vector and otherwise zero. Z is the number of formula units in the

primitive unit cell and included as a scaling factor to compare JDOS for the structures with different Z . The equation of the linewidth in Eq. (1) contains terms of $(n_{\lambda'} + n_{\lambda''} + 1)$ and $(n_{\lambda'} - n_{\lambda''})$. Thus in more rigorous study, instead of $D_2^{(1)}$ and $D_2^{(2)}$, we should employ weighted JDOS with these terms. We firstly employ the JDOS in Eq. (6) to intuitively examine the similarity between the linewidths of the α and β phases. The weighted JDOS (WJDOS) will be briefly shown later including that of the γ phase.

Fig. 6 shows frequency-functions of JDOS at several different \mathbf{q} -points. They have very weak \mathbf{q} -point dependences. At the low frequency region up to $\simeq 10$ THz $D_2^{(1)}$ is dominant between the two terms. The $D_2^{(1)}$ are similar between the phases. In the present Si_3N_4 system, the phonon modes of the acoustic and low-frequency optical branches, which largely contribute to the κ , are much fewer than the other phonon modes. The JDOS are mainly determined by the latter majorities. As in the band diagrams, the branches of the majorities are rather flat. Thus we can approximately disregard in Eq. (6) the dependences of the $\omega_{\lambda'}$ and $\omega_{\lambda''}$ on the \mathbf{q}' and \mathbf{q}'' . In this case $D_2^{(1)}$ is simplified to the half part ($\omega \geq 0$) of the auto-correlation function of DOS. The DOS for both of the α and β phases in Fig. 5-a have a frequency gap. The $D_2^{(1)}$ reflect this DOS feature, dropping suddenly around 0 THz and showing a small shoulder around 5 THz, corresponding to the width of the gap. Because the gap is originated from the local modes of the planer NSi_3 composing each of the α and β crystal structures,⁴² the $D_2^{(1)}$ are similar in these phases.

The WJDOS are shown in Fig. 7. The terms corresponding to $D_2^{(1)}$ and $D_2^{(2)}$ are denoted as $N_2^{(1)}$ and $N_2^{(2)}$. They are weighted $D_2^{(1)}$ and $D_2^{(2)}$ with $(n_{\lambda'} - n_{\lambda''})$ and $(n_{\lambda'} + n_{\lambda''} + 1)$, respectively. For the comparison among the three phases, we only show the frequency distributions at $\mathbf{q} = (0,0,0)$ because the \mathbf{q} dependences of the WJDOS were as weak as JDOS. The weighting factors reduce the $N_2^{(1)}$ near 0 THz and enhance the $N_2^{(2)}$ in the high frequency range. The latter reduces the $d\kappa^c/d\omega$ in the high frequency range, for all the phases. The total WJDOS are similar between the α and β phases. The γ phase has slightly small intensities of the total WJDOS below ~ 10 THz.

TABLE III. Averages of $|\Phi_{\lambda\lambda'\lambda''}|^2$ over frequency ranges of ω_λ (0–15 and 0–35 THz) and all (λ', λ'') . The values are in units of $10^{-9} \text{ eV}^2 \text{ f.u.}^2$.

| Frequency Range (THz) | Phase | | |
|-----------------------|----------|---------|----------|
| | α | β | γ |
| 0–15 | 1.1 | 1.1 | 2.3 |
| 0–35 | 5.2 | 5.2 | 4.6 |

As for $|\Phi_{\lambda\lambda'\lambda''}|^2$, in Table. III, they are averaged over two kinds of frequency ranges of 0–15 or 0–35 THz for ω_λ

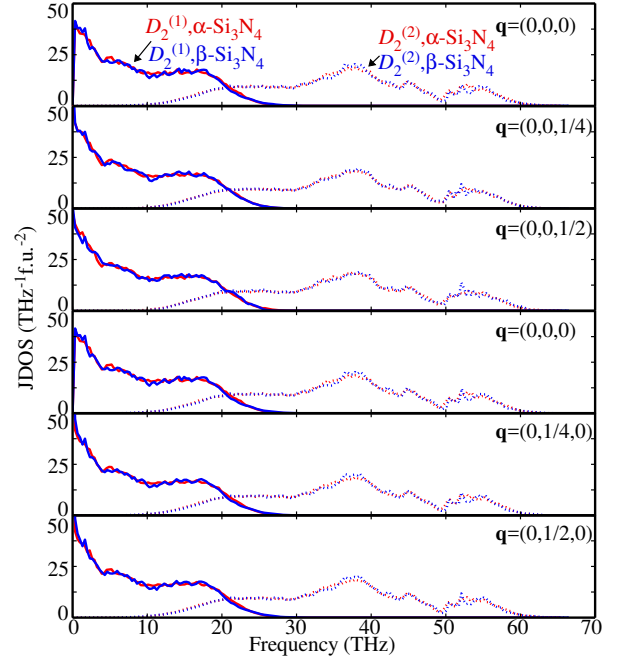


FIG. 6. (color online) JDOS of α - and β - Si_3N_4 at different \mathbf{q} points. The first and forth rows are JDOS at the same Γ -point but calculated with the polarization for non-analytic term correction set along c^* and b^* , respectively.

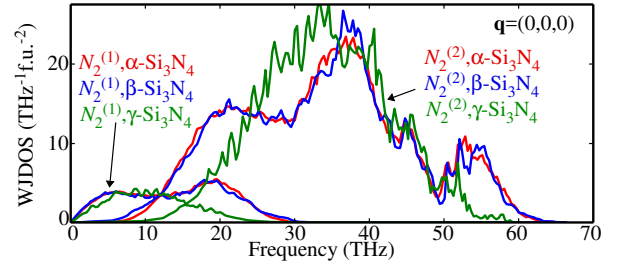


FIG. 7. (color online) Comparison of WJDOS at $\mathbf{q} = (0,0,0)$ for 300 K among the three phases.

and all indices in λ' and λ'' . The averages are very similar values between the α and β phases. With the similar impacts of the (W)JDOS and $|\Phi_{\lambda\lambda'\lambda''}|^2$, the linewidths in these phases are similar. For the γ phase, the large $|\Phi_{\lambda\lambda'\lambda''}|^2$ attribute to the large linewidths. We set the frequency ranges for ω_λ so that the narrower frequency range approximately corresponds to the range where the phonon modes largely contribute to the κ . A small change in the frequency ranges by a few THz did not change the qualitative characters of the averages.

Finally, we examine the exceptional, but striking difference in linewidth distributions between the α and β phases: In the α phase, Γ_λ below ~ 5 THz are aligned on a single smooth line, while in the β phase, they are scattered roughly on two branches. This difference is investigated by trying to relate the linewidths with the directions of the atomic vibrations of the phonon modes.

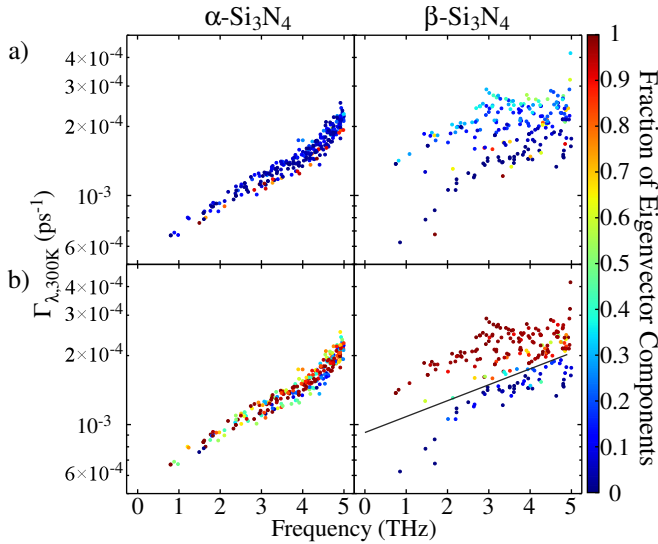


FIG. 8. (color online) Distribution of linewidths $\omega_{\lambda} \leq 5$ THz with colors with respect to strengths of eigenvector components along \mathbf{q} (a) and on ab plane (b).

Fig. 8 enlarges the $(\Gamma_{\lambda}, \omega_{\lambda})$ plots in this frequency range. In Fig. 8-a, the Γ_{λ} are classified using colors according to the sums of the squares of the eigenvector components along the \mathbf{q} ; the sum is 1 for a perfectly longitudinal wave. However, these sums show no clear contrast between the two branches in the β phase. Fig. 8-b shows the same plot as Fig. 8-a, but with colors according to the sums of the squares of the eigenvector components along the ab plane, which is 1 when the eigenvector lays on the ab plane. There is a tendency in the β phase that Γ_{λ} are large for atomic vibrations along the ab plane. This means that the vibration modes along the ab plane, belonging to the acoustic phonon branches, are more easily scattered in the β phase, no matter whether they are longitudinal or transverse. For the panel of β -Si₃N₄ in Fig. 8-b, a straight line splits the phonon modes to two groups. The numbers of the phonon modes assigned to the larger and smaller Γ_{λ} groups are 157 and 58, whose ratio is confirmed close to the population ratio of the vibration modes along and out of the ab plane.

IV. SUMMARY

In the present study, we investigate the lattice thermal conductivities of the three Si₃N₄ phases, by using the lattice dynamics based on the first principles interatomic force constants. The main remarks are as follows:

1) In the α - and β -Si₃N₄, whose crystal structures are characterized by the stacking manners of the basal layer

structures, which largely alter κ , due to the folding effects of the band gaps and anticrossings. This contrasts with the case of the zincblende and wurtzite structures in the previous study¹⁵. The κ of α -Si₃N₄ is rather isotropic, while the κ_{zz} of the β phase is twice or more larger than the other κ_{ii} of the three phases.

2) In the α phase, the acoustic mode phonons below 6 THz are the main heat carriers, while in the β phase, the phonons below 12 THz contribute to the κ . Their group velocities are confirmed to characterize the behaviours of κ .

3) In the γ phase, the frequency distribution of the phonon mode contributions to κ is similar to that for κ_{xx} of β -Si₃N₄. Its large phonon-phonon scattering strength and steep longitudinal acoustic branches attribute to this.

ACKNOWLEDGMENTS

The present work was partly supported by Grants-in-Aid for Scientific Research of MEXT, Japan (Grant No. 15K14108 and ESISM (Elements Strategy Initiative for Structural Materials) of Kyoto University).

Appendix A: Pressure dependence of lattice thermal conductivity of γ -phase

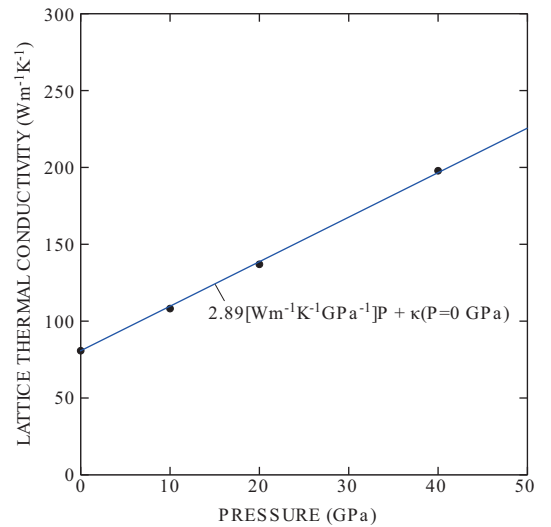


FIG. 9. (color online) Pressure dependence of lattice thermal conductivity of γ -Si₃N₄.

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