

# First-principles calculation of the lattice thermal conductivities of $\alpha$ -, $\beta$ -, and $\gamma$ - $\text{Si}_3\text{N}_4$

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Lattice thermal conductivities of  $\alpha$ -,  $\beta$ - and  $\gamma$ - $\text{Si}_3\text{N}_4$  single crystals 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  $\beta$ - $\text{Si}_3\text{N}_4$  is calculated as  $\kappa_{xx} = 73$  and  $\kappa_{zz} = 198$  (in units of  $\text{Wm}^{-1}\text{K}^{-1}$ ), that is consistent with the reported experimental values of 69 and 180, respectively. For  $\alpha$ - $\text{Si}_3\text{N}_4$ ,  $\kappa_{xx} = 69$  and  $\kappa_{zz} = 99$  are obtained. The difference of anisotropy between  $\alpha$ - $\text{Si}_3\text{N}_4$  and  $\beta$ - $\text{Si}_3\text{N}_4$  is originated from their characteristic difference in the phonon band structures, although their crystal structures are similar in their local atomic coordinates. In  $\alpha$ - $\text{Si}_3\text{N}_4$ , acoustic-mode phonons below 6 THz are the main heat carriers. In  $\beta$ - $\text{Si}_3\text{N}_4$ , the phonon modes up to 12 THz contribute to the lattice thermal conductivity. In  $\gamma$ - $\text{Si}_3\text{N}_4$ ,  $\kappa = 81$  is obtained. The distribution of phonon mode contributions to lattice thermal conductivity with respect to phonon frequency is found to closely resemble  $\kappa_{xx}$  of  $\beta$ - $\text{Si}_3\text{N}_4$  although the phonon lifetimes of  $\gamma$ - $\text{Si}_3\text{N}_4$  are twice shorter than those of  $\beta$ - $\text{Si}_3\text{N}_4$ .

## I. INTRODUCTION

Several nitride insulators are known to exhibit high thermal conductivities and are important for heat transfer materials at elevated temperatures. For example, Slack *et al.*<sup>1</sup> reported that wurtzite-type w-AlN has thermal conductivity of  $\gg 100 \text{ Wm}^{-1}\text{K}^{-1}$ .  $\text{Si}_3\text{N}_4$  has become another promising thermal conductive insulator as its thermal conductivity has been improved up to  $177 \text{ Wm}^{-1}\text{K}^{-1}$  by using the advanced ceramic technologies related to the densification and microstructure control.<sup>2-5</sup> Since the  $\text{Si}_3\text{N}_4$  ceramics also exhibit high mechanical strength at elevated temperatures, they are regarded as ideal materials for the use in various applications, such as engine components, gas turbines, and heat sink substrates of power semiconductor devices.

At atmospheric pressure,  $\text{Si}_3\text{N}_4$  exists in one of two phases,  $\alpha$  and  $\beta$ , which are generally considered as low- and high-temperature phases, respectively.<sup>2,5,6</sup> Their crystal structures belong to the space groups of P31c and P6<sub>3</sub>/m, respectively.<sup>7,8</sup> These structures have different stacking orders of equivalent basal layer structures originated by  $\text{SiN}_4$  tetrahedra.<sup>9</sup> In Fig.1 these layer structures are depicted from the principal direction, as A, B, C, and D in the  $\alpha$  phase and A and B in the  $\beta$  phase. The stacking manners in  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$  are thus as ABCDABCD.. and ABAB.., respectively. The  $\alpha$  phase has additional two layer structures of C and D, which are related to the A and B by the *c* glide operation.<sup>9</sup> Along this direction the lattice constant of the  $\alpha$  phase is approximately two times longer than that of the  $\beta$  phase.

The reported values<sup>2-5,11</sup> of the thermal conductivity of the  $\text{Si}_3\text{N}_4$  polymorphs were measured on polycrystalline bulk samples. These values were significantly af-

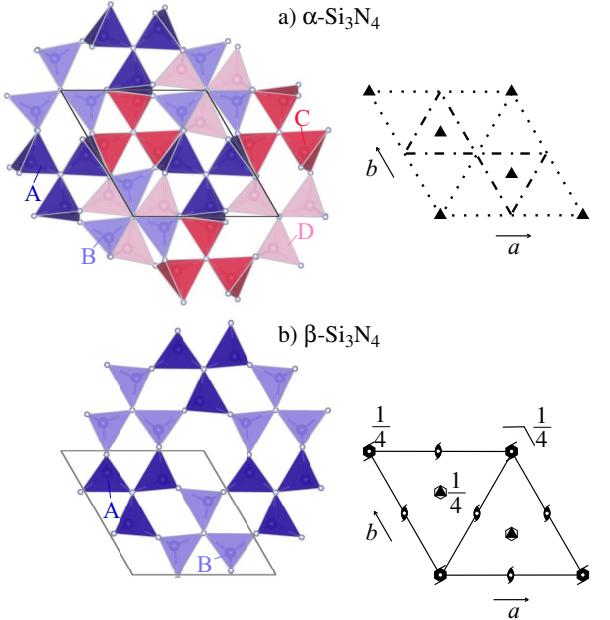


FIG. 1. (color online) Crystal structures of  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$ . Stacking of  $\text{SiN}_4$  tetrahedron layers are shown in left. (a) ABCDABCD.. for  $\alpha$ - $\text{Si}_3\text{N}_4$ . (b) ABAB.. for  $\beta$ - $\text{Si}_3\text{N}_4$ . Space group diagrams<sup>10</sup> in P31c ( $\alpha$ - $\text{Si}_3\text{N}_4$ ) and P6<sub>3</sub>/m ( $\beta$ - $\text{Si}_3\text{N}_4$ ) are shown in right.

fected by the contained lattice defects, impurities, shapes and orientations of the constituent crystal grains;<sup>12</sup> the thermal conductivity intrinsic to a defect-free single crystal has not been established. As an experimental access to the intrinsic thermal conductivity, Li *et al.*<sup>13</sup> applied high-resolution thermoreflectance microscopy to a single  $\beta$ - $\text{Si}_3\text{N}_4$  grain in a ceramic sample. The analyzed

thermal conductivities were 69 and 180 Wm<sup>-1</sup>K<sup>-1</sup> along the *a* and *c* axes, respectively. These thermal quantities correspond to the diagonal elements  $\kappa_{xx}$  and  $\kappa_{zz}$  of the lattice thermal conductivity tensor  $\kappa$ . We consider the anisotropy of  $\kappa_{zz}/\kappa_{xx} \sim 3$  is relatively large. Theoretically, Hirosaki *et al.*<sup>12</sup> estimated  $\kappa$  by applying the Green-Kubo formulation to the molecular dynamics (MD) method with the interatomic potentials proposed by Vashishta *et al.*<sup>14</sup>. They calculated  $\kappa_{xx}$  and  $\kappa_{zz}$  of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> as 105 and 225 Wm<sup>-1</sup>K<sup>-1</sup>, and those of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> as 170 and 450 Wm<sup>-1</sup>K<sup>-1</sup>, respectively. The ratio  $\kappa_{zz}/\kappa_{xx}$  in  $\beta$ -Si<sub>3</sub>N<sub>4</sub> agreed well with the experimental results obtained by Li *et al.*<sup>13</sup>: The  $\kappa_{ii}$  values overestimated the experimental by more than two times.

On many polymorphs of the wurtzite and zincblende structures, the lattice thermal conductivities were recently calculated based on a first principles calculation and Boltzman transport theory.<sup>15</sup> These polymorphs have different stacking orders of the densest atom planes as ABAB.. and ABCABC... The different stacking orders merely altered the lattice thermal conductivities.<sup>15</sup> The phonon linewidth distribution and phonon density of states were similar between the structures as well.<sup>15</sup> On the other hand, the previous MD results on  $\alpha$ - and  $\beta$ -Si<sub>3</sub>N<sub>4</sub> presented that the different stacking orders in these phases altered the  $\kappa$  values largely. The large difference has not been clarified based on the microscopic phonon properties. It is interesting to investigate it using the same approach as in Ref.15 for  $\alpha$ - and  $\beta$ -Si<sub>3</sub>N<sub>4</sub>.

In addition to the  $\alpha$  and  $\beta$  phases, a cubic spinel phase ( $\gamma$ -Si<sub>3</sub>N<sub>4</sub>) is known to form upon compression and in-situ heating.<sup>16,17</sup> The reported transition pressures were scattered from 10 to 36 GPa depending on the experimental conditions.<sup>18</sup> The  $\gamma$  phase is experimentally quenched to atmospheric pressure at room temperature. Its thermal conductivity has not been experimentally reported; it has been estimated only by the Slack model.<sup>19</sup>

The present study aims to qualitatively understand the lattice thermal conductivity tensors among the three Si<sub>3</sub>N<sub>4</sub> phases by means of the first principles approach. We calculate  $\kappa$  of the  $\gamma$  phase as well, for systematic understanding of the lattice thermal conductivity in the Si<sub>3</sub>N<sub>4</sub> system. After the methodology section, we examine the validity of the present results first. Our calculated thermal properties are compared with the available experimental and theoretical references. Then we investigate the characteristics in the calculated  $\kappa$  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 approx-

imation (single-mode RTA). We also tried the direct solution of LBTE<sup>20</sup> and leave its calculated  $\kappa$  values in the following section. The difference in the calculated  $\kappa$  between by the single-mode RTA and by the direct solution was found minor for our discussion. Therefore we limited our research to use the single-mode RTA to take advantage of its intuitive closed form of  $\kappa$ .

In the following sections, we denote a 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 reciprocal of linewidth,  $\tau_{\lambda,ph-ph} = (2\Gamma_{\lambda})^{-1}$ , where the linewidth that we employed in this study is as follows:

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

Here  $\omega_{\lambda}$  is the harmonic phonon frequency of the phonon mode  $\lambda$ ,  $n_{\lambda} = [\exp(\hbar\omega_{\lambda}/k_B T) - 1]^{-1}$  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 usual coordinate transformation of third-order force constants from direct space to phonon space.<sup>15</sup> The second- and third-order real-space force constants were obtained from the *ab-initio* calculation, whose details are written in the next section.

In order to compare the more realistic results of the calculated  $\kappa$  with the experimental data, the isotopic scattering effect due to the natural isotope distribution was taken into account according to the second-order perturbation theory.<sup>21</sup> With the relaxation times of the phonon-phonon scattering and isotopic scattering,  $\tau_{\lambda,ph-ph}$  and  $\tau_{\lambda,iso}$ , the total relaxation time for a phonon mode was assumed to be  $1/\tau_{\lambda} = 1/\tau_{\lambda,ph-ph} + 1/\tau_{\lambda,iso}$ , according to Matthiessen's rule.

The available experimental thermal conductivity data of the Si<sub>3</sub>N<sub>4</sub> system have been measured on the polycrystalline samples and not measured from any single crystals. In order to consider the effect of various lattice defects in the polycrystalline samples, such as grain boundaries, impurities, and vacancies, we crudely took them into account by a relaxation time  $\tau_{\lambda,bs} = L/|\mathbf{v}_{\lambda}|$  of a phonon boundary scattering model, where  $\mathbf{v}_{\lambda} = \nabla_{\mathbf{q}}\omega_{\lambda}$  is the group velocity and  $L$  a parameter regarding to the boundary mean free path. We consider  $\tau_{\lambda,bs}$  as a variable parameter and included it to  $\kappa$  according to Matthiessen's rule.

The closed form of  $\kappa$  within 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,  $\Omega$  is the unit cell volume, and  $c_{\lambda}$  is the mode heat capacity. To analyze  $\kappa$  in

detail, we calculate the cumulative thermal conductivity:

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

and its derivative  $\frac{\partial \kappa^c(\omega)}{\partial \omega}$  to see the phonon mode contributions to  $\kappa$ .

The lattice thermal conductivities were calculated with the phonon-phonon interaction calculation code PHONO3PY<sup>15</sup>, while the harmonic phonon states were analyzed with the phonon calculation code PHONOPY<sup>22</sup>.

## B. Computational details

The force constants were calculated using the first-principles projector augmented wave method<sup>23</sup> (VASP code<sup>24–26</sup>). The generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof<sup>27</sup> was used for the exchange correlation potential. A plane wave energy cutoff of 500 eV was employed. The crystal structures were optimized until the residual forces acting on the constituent atoms was less than  $10^{-6}$  eV/Å. The structural optimization was firstly performed for a temperature of 0 K and 0 GPa. Here the temperature and pressure were considered only for the electronic system and the zero point lattice vibration was not taken into account. The calculated lattice parameters were  $a = 7.808$  Å and  $c = 5.659$  Å for the  $\alpha$  phase,  $a = 7.660$  Å and  $c = 2.925$  Å for the  $\beta$  phase, and  $a = 7.787$  Å for the  $\gamma$  phase, which agree with the experimental data<sup>7,8,28</sup> within +0.7 % errors. The lattice volume optimized within the local density approximation (LDA)<sup>29</sup> for the exchange correlation potential was, for  $\beta\text{-Si}_3\text{N}_4$ , 3 % smaller than within GGA, which is a typical volume contraction of LDA. The  $\kappa$  calculated within LDA was larger by 2.6 % than within GGA. For our discussion, this difference is enough small, therefore the impact of choice of exchange correlation potential is considered to be minor in our study.

Supercell and finite difference approaches were used to calculate the force constants.<sup>30</sup> The supercells were  $1 \times 1 \times 2$ ,  $1 \times 1 \times 3$ , and  $1 \times 1 \times 1$  supercells of the conventional unit cells for the calculation of the third-order force constants in  $\alpha$ ,  $\beta$ , and  $\gamma\text{-Si}_3\text{N}_4$ , respectively; they were  $3 \times 3 \times 4$ ,  $3 \times 3 \times 8$  and  $2 \times 2 \times 2$  for the second-order force constants. The length of the induced atomic displacement was set to 0.03 Å. Table I shows the  $\kappa$  calculated with several different sets of the supercells, indicating that our calculated  $\kappa$  is reasonably converging with respect to the size of the supercells.

Non-analytical term correction<sup>31</sup> was applied to the second-order force constants to take into account the long range Coulomb forces present in ionic crystals. For the correction, Born effective charges were calculated by using the density functional perturbation theory

TABLE I. Calculated lattice thermal conductivities of  $\alpha$ -,  $\beta$ -, and  $\gamma\text{-Si}_3\text{N}_4$  ( $\text{WK}^{-1}\text{m}^{-1}$ ) at 300 K with respect to several combinations of supercell sizes.

Phase	Supercell (# of atoms)		LTC	
	3 <sup>rd</sup> force constants	2 <sup>nd</sup> force constants	<i>xx</i>	<i>zz</i>
$\alpha$	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
$\beta$	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
$\gamma$	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	

## (DFPT).Ref!

Uniform  $\mathbf{k}$ -point sampling meshes of  $4 \times 4 \times 2$ ,  $4 \times 4 \times 3$ , and  $3 \times 3 \times 3$  were used for the third-order force constants of the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases. For the  $\alpha$  and  $\beta$  phases the center of the  $a^* \text{-} b^*$  plane was sampled while the center on the  $c^*$ -axis was not. For the  $\gamma$  phase, non- $\Gamma$  center mesh was used. For the second-order force constants, the  $\Gamma$ -point was only sampled for the  $\alpha$  and  $\beta$  phase and the only one  $\mathbf{k} = (0.5, 0.5, 0.5)$  point was sampled for the  $\gamma$  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 used to calculate  $\kappa$  in Eq. (2) for the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases.

We examined the effect of thermal expansion on  $\kappa$  by calculating them with the crystal structures optimized for several finite temperatures within the quasi-harmonic approximation (QHA)<sup>32</sup>. The structure was optimized for a temperature and 0 GPa so as to show a minimum Helmholtz free energy.  $\kappa$  for the temperature was calculated with the optimized structure. This  $\kappa$  was differed from the one for the temperature, calculated with the structure optimized for 0 K and 0 GPa. We consider that this difference is caused by the thermal expansion of the lattice. For  $\beta\text{-Si}_3\text{N}_4$  and the temperatures of 300, 600, 900, 1200, and 1500 K, the differences in  $\kappa$  between the two structures were found less than 1 %, similar to the case of Si and Ge<sup>33</sup>. For the present study, these differences are negligible and we adopt the  $\kappa$  calculated with the structure optimized for 0 K and 0 GPa.

We calculated the volumetric thermal expansion coefficients and compared them with the reported experimental values so as to check the validity of the present thermal conductivity calculation, because the thermal expansion is originated from the anharmonicity of the interatomic potential as well as  $\kappa$ . The calculated val-

ues of the  $\alpha$  and  $\beta$  phases are  $4.31 \times 10^{-6}$  and  $4.19 \times 10^{-6} \text{ K}^{-1}$  for 300 K, while the experimental values were 3.75 and  $3.55 (10^{-6} \text{ K}^{-1})^{34}$ . The present calculation reproduced the experimental tendency where the  $\alpha$  phase has a slightly larger thermal expansion coefficient than the  $\beta$  phase, supporting that the present calculations enable us to qualitatively compare the calculated  $\kappa$  of the  $\text{Si}_3\text{N}_4$  phases.

In order to compare the microscopic phonon properties among the three phases at the same conditions, those results calculated at 0 GPa are shown and discussed. For the  $\gamma$  phase, this means that we assume the condition of virtually quenched  $\gamma$  phase at 0 GPa from the high pressure. To examine the analytical continuity of the properties with respect to pressures, we calculated  $\kappa$  of  $\gamma$  phase at 10, 20, and 40 GPa as shown in Fig. 8, where the phenomenological behaviour of linear dependence of  $\kappa$  with respect to pressure with the calculated slope of  $2.89 \text{ Wm}^{-1}\text{K}^{-1}\text{GPa}^{-1}$  was reproduced as similar to Ref. 35. By this, we consider that the microscopic values are also varied smoothly with the pressure and those at 0 GPa are valuable to compare with the  $\alpha$  and  $\beta$  phases.

### C. Direct solution of LBTE

The merit to employ the single-mode RTA for thermal conductivity calculation is the closed form, by which we can intuitively understand the qualitative character of  $\kappa$  in terms of the relaxation time and group velocity. The microscopic understanding of the full solution of LBTE is still under the development<sup>36</sup> and the microscopic picture based on collective phonons<sup>37</sup> will require more complicated investigation although it is known that the single-mode RTA solution of LBTE often underestimates the full solution.<sup>33,38</sup>

For the  $\alpha$  and  $\beta$  phases, we adopted a direct solution of LBTE<sup>20</sup>, which is one of the methods of LBTE full solutions. Its  $\kappa_{xx}$  and  $\kappa_{zz}$  without the isotope effect were 69 and  $102 \text{ Wm}^{-1}\text{K}^{-1}$  for the  $\alpha$  phase and 76 and  $238 \text{ Wm}^{-1}\text{K}^{-1}$  for those of the  $\beta$  phase, respectively, while the corresponding single-mode RTA values were 70 and  $102 \text{ Wm}^{-1}\text{K}^{-1}$  for the  $\alpha$  phase and 76 and  $210 \text{ Wm}^{-1}\text{K}^{-1}$  for the  $\beta$  phase. The  $\kappa_{zz}$  of the direct solution in the  $\beta$  phase was 13 % larger than that of the single-mode RTA solution. Since the differences in  $\kappa$  between the LBTE solutions are not significant, we expect the physics on those lattice thermal conductivities is well understood within RTA in the current level of our interest. **Therefore, we discuss the results of the thermal conductivities calculated using the single-mode RTA solution.**

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, compared with the experimental data. Theoretical bulk moduli  $B$  in units of GPa, calculated by the authors by using the present band method, are presented in the fourth column.

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

<sup>a</sup> Ref. 19, Slack model.

<sup>b</sup> Ref. 12, molecular dynamics (Green-Kubo).

<sup>c</sup> Ref. 13, single crystalline grains of poly-crystals.

## III. RESULTS AND DISCUSSION

### A. Lattice thermal conductivities

Table II shows the present theoretical  $\kappa$  values at 300 K. The  $\kappa_{ii}$  of  $\beta\text{-Si}_3\text{N}_4$  are markedly more anisotropic than those of  $\alpha\text{-Si}_3\text{N}_4$ . The directional averages  $\sum_i \kappa_{ii}/3$  are 79, 115, and 77  $\text{Wm}^{-1}\text{K}^{-1}$  for the  $\alpha$ ,  $\beta$ ,  $\gamma$  phases, respectively. The value of the  $\gamma$  phase is similar to that of the  $\alpha$  phase, in spite of comparatively large difference between the bulk moduli ( $B$ ) that are also shown in Table II.

Table II also shows the previously reported experimental<sup>13</sup> and theoretical<sup>12</sup>  $\kappa_{ii}$  for the references. For the  $\beta$  phase, our  $\kappa_{ii}$  agrees better with the experimental, than that of the molecular calculation<sup>12</sup> does. The Slack model was employed by Morelli *et al.*<sup>19</sup>. Their results are shown as  $\kappa$  in Table II. For the  $\beta$  phase, our directional average agrees better with the experimental  $\sum_i \kappa_{ii}/3$ , compared with the  $\kappa$  in the Slack model.

Fig. 2 shows the theoretical  $\kappa_{ii}$  of the  $\alpha$  and  $\beta$  phases as a function of  $T$ , together with the reference experimental data<sup>5,11,13</sup>. The thermal conductivities for a series of temperatures were only reported on the polycrystalline bulk samples. These bulk thermal conductivities cannot be directly compare with the calculated  $\kappa$  because the microstructures of the bulk samples largely affected the thermal conductivities: **For largely anisotropic  $\kappa_{ii}$ , the thermal conductivities were deviated from the simple directional average of the  $\kappa_{ii}$ , depending on the shapes of the constituent crystal grains.** We took into account this effect by using a parameter  $0 \leq w \leq 1$  and fitting  $w\kappa_{xx} + (1 - w)\kappa_{zz}$  to the experimental  $\kappa$  by the least squares method.

In Fig. 2, the  $\kappa_{ii}$  calculated without  $\tau_{\lambda,\text{bs}}$  is nearly inversely proportional to  $T$  because  $n_\lambda$  in Eq. (1) can be reduced to  $\exp(-\hbar\omega_\lambda/k_B T)$ . In Fig. 2-a, the temperature dependence of the experimental data of a chemically vapor-deposited  $\alpha\text{-Si}_3\text{N}_4$  sample<sup>11</sup> is deviated from inverse proportion considerably, intersecting the theoretical curves. Thus no value of  $w$  adjusts the theoretical LTC to the experimental curve. The full solution

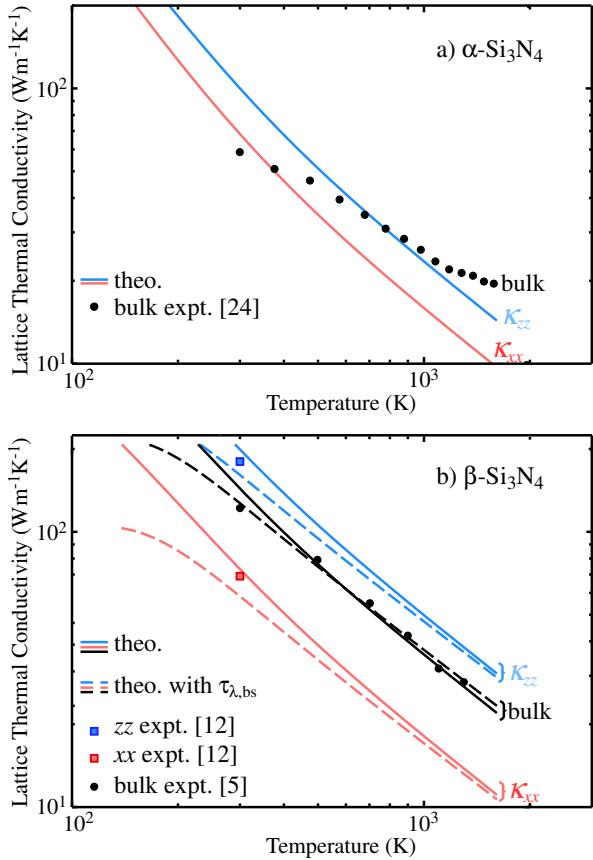


FIG. 2. (color online) Temperature dependence of LTC for  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$ . For  $\beta$ - $\text{Si}_3\text{N}_4$ , the LTC with the boundary scattering effect are shown by broken curves. Theoretical LTC for the bulk  $\beta$ - $\text{Si}_3\text{N}_4$  sample are also shown to be compared with the experimental data of the bulk sample.

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 according to Matthiessen's rule, could not explain the discrepancy as well. A  $L$  value of  $0.6 \mu\text{m}$ , which was much smaller than the experimental grain size  $10 \mu\text{m}$ , decreased the room-temperature theoretical  $\kappa_{xx}$  and  $\kappa_{zz}$  values toward the experimental values, but severely underestimated the experimental values at the high temperature side. At present, the reason for the discrepancy between the theoretical and experimental behaviors is unclear. Although the crystal structure of the experimental sample was characterized as  $\alpha$ - $\text{Si}_3\text{N}_4$ , significant lattice defects might exist in the as-deposited sample as pointed out by Hirosaki *et al.*<sup>12</sup> and the simple phonon boundary scattering model might fail to describe their effects.

The experimental  $\kappa$  of the  $\beta$  phase ceramic bulk<sup>5</sup> as plotted with solid circles in Fig. 2-b fall well between the theoretical  $\kappa_{xx}$  and  $\kappa_{zz}$ , being nearly inversely proportional to  $T$ . Simple directional averages of the theoretical  $\kappa_{ii}$  slightly underestimate these experimental bulk

thermal conductivities. This fact is understood from the experimentally tailored microstructure containing large  $\beta$ - $\text{Si}_3\text{N}_4$  grains selectively grown along the  $c$  axis.<sup>5</sup> The theoretical bulk thermal conductivities were fit well with  $w = 0.44$  to the experimental bulk thermal conductivities. For the effects of lattice defects most of which were grain boundaries, we included  $\tau_{\lambda,\text{bs}}$  with  $L = 0.6 \mu\text{m}$  to further fit the theoretical curve ( $w = 0.33$ ) to the experimental data. The  $L$  value is slightly smaller than the average grain size ( $2 \mu\text{m}$ )<sup>5</sup> of the experimental polycrystalline sample. The experimental  $\kappa_{xx}$  and  $\kappa_{zz}$  for room temperature are also plotted by filled squares, which are in-between the theoretical tensor elements with and without  $\tau_{\lambda,\text{bs}}$ .

## B. Dispersion curves

Figure 3 shows the phonon band diagrams of the three  $\text{Si}_3\text{N}_4$  phases. The entire band diagrams are almost identical to those reported earlier<sup>18,39</sup>. However, here we investigate the group velocities projected on the high-symmetry paths, especially focusing on the anisotropy in the group velocities of the  $\alpha$  and  $\beta$  phases. This was not investigated by the previous works.

The calculated  $\omega_{\lambda}$  are much more increased in the  $\beta$  phase on the acoustic branches from  $\Gamma$  to  $A$  than to  $K$  or  $M$ . This is different from the case of the  $\alpha$  phase; those are increased from  $\Gamma$  to  $A$ ,  $K$ , and  $M$  similarly. This difference in the increments of  $\omega_{\lambda}$  between the two phases is because the  $\Gamma$ - $A$  path length of the  $\beta$  phase is approximately twice that of  $\alpha$ ; the lattice constant  $c$  of  $\beta$  is nearly half that of  $\alpha$ , owing to the difference in the stacking manner of the basal layers. Normally, optical branches are flat; however, the upper branches along the  $\Gamma$ - $A$  path also have significantly large  $v_{\lambda,z}$ . These findings on the phonon branches indicate that the  $\beta$  phase contains a larger number of phonon modes whose group velocity is large and oriented along the  $c^*$  axis. We will show this tendency in the next section.

In Fig. 3-c for the  $\gamma$  phase, the acoustic phonon branches show significant linear dispersions on the  $\Gamma$ - $L$  and  $\Gamma$ - $X$  paths. The roughly constant gradients of  $\omega_{\lambda}$  are large, reflecting the large elastic constants of the  $\gamma$  phase as shown in Table II.

## C. $\omega_{\lambda}$ counter map on reciprocal plane

In another point of view on  $\mathbf{v}_{\lambda}$ , Fig. 4 shows the  $\omega_{\lambda}$  distribution on the  $b^*-c^*$  plane within the Brillouin-zones of the  $\alpha$  and  $\beta$  phases. The distributions on the other planes containing the  $c^*$  axis did not differ much. Thus, we selected the  $b^*-c^*$  plane as a representative one. We show the  $\omega_{\lambda}$  distributions for four modes from the lowest frequency because they contribute significantly to  $\kappa$ . Fig. 4-a for the  $\alpha$  phase shows that the distributions of the  $\omega_{\lambda}$  are fairly isotropic. Their gradients, the group ve-



FIG. 3. (color online) Brillouin-zones (left) and calculated phonon band diagrams (right) for three  $\text{Si}_3\text{N}_4$  phases.

locities projected onto the  $b^*-c^*$  plane, are thus isotropic. On the other hand, in Fig. 4-b for the  $\beta$  phase, the iso-frequency lines in  $0.06 \leq q_{c^*} \leq 0.12 (\text{\AA}^{-1})$  are rather parallel to the  $q_{b^*}$  axis, indicating that the four modes of the  $\beta$  phase, in a significantly large part of the Brillouin zone, have group velocities oriented along the  $c$  axis.

#### D. Frequency-dependences of $\kappa^c$ , $v_\lambda$ and $\Gamma_\lambda$

In order to rigorously evaluate the contribution of the microscopic phonon properties to  $\kappa$ , we examine the microscopic phonon properties taken over the Brillouin zone. In Fig. 5 are shown phonon densities of states (DOS), cumulative thermal conductivities and their frequency derivatives, DOS weighted with the squares of the group velocity components,  $v_{\lambda,x}^2$  and  $v_{\lambda,z}^2$ , and distributions of the phonon linewidths.

The arrow in Fig. 5-a indicates the frequency position of the first peak in DOS. The peak was composed of the acoustic phonon modes near the Brillouin zone boundary by the effect of a Van Hove singularity. This is confirmed

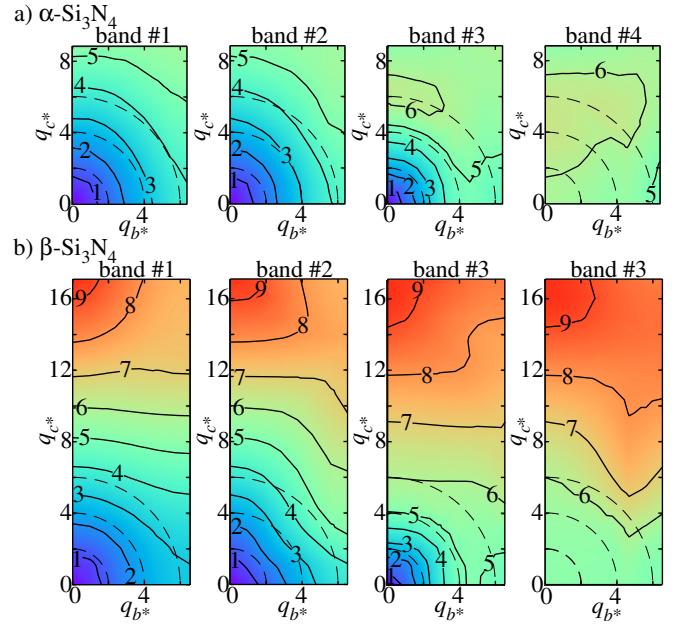


FIG. 4. (color online) Contour maps of phonon frequency (THz) on the  $b^*-c^*$  planes of Brillouin-zones. The maps for the four lowest-frequency phonon states are shown. The frequency landscapes are formed by simply connecting the frequencies of the same band indices, assigned by ascending order of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

by revisiting the band structures in Fig. 3. The dispersions of the acoustic branches are rather small on the A-H-K and M-L-H paths for the  $\alpha$  and  $\beta$  phases and the W-L and X-W-K paths for the  $\gamma$  phase. The branches roughly stay around the frequency of the DOS peak. The frequency derivatives of  $\kappa_{ii}^c$  are still significantly large in the frequency range from the DOS peak position to a few THz higher than that. frequency goes over the DOS peak position. above the DOS peak position only for the  $\beta$  phase. Almost half of the contribution to  $\kappa_{zz}$  is above the DOS peak position. This indicates that the low-frequency optical phonons significantly contribute to  $\kappa_{zz}$ . The origin of the remarkable contribution is their large  $v_{\lambda,z}$ . This is consistent with the weighted DOS in Fig. 5-c. The weighted DOS for  $v_{\lambda,z}$  and the  $\beta$  phase is large above the DOS peak indication is in accordance with their large dispersions on the  $\Gamma$ -A path in the band structure in Fig. 3-b.

$\kappa^c$  in the  $\gamma$  phase resembles closely to  $\kappa_{xx}^c$  in the  $\beta$  phase, although the linewidths of the  $\gamma$  phase are twice larger than those of the  $\beta$  phase. Because of the large differences in the crystal structure and the phonon properties in Figs. 5-a,c,d of the  $\gamma$  phase from the  $\alpha$  and  $\beta$  phases, we hereafter focus on the comparison between the latter two phases.

In Figs. 5-b and c, the directional differences in the derivatives of  $\kappa_{ii}^c$  in the  $\alpha$  and  $\beta$  phases are qualitatively well consistent with the directional differences in the weighted DOS. The relatively larger intensities in the

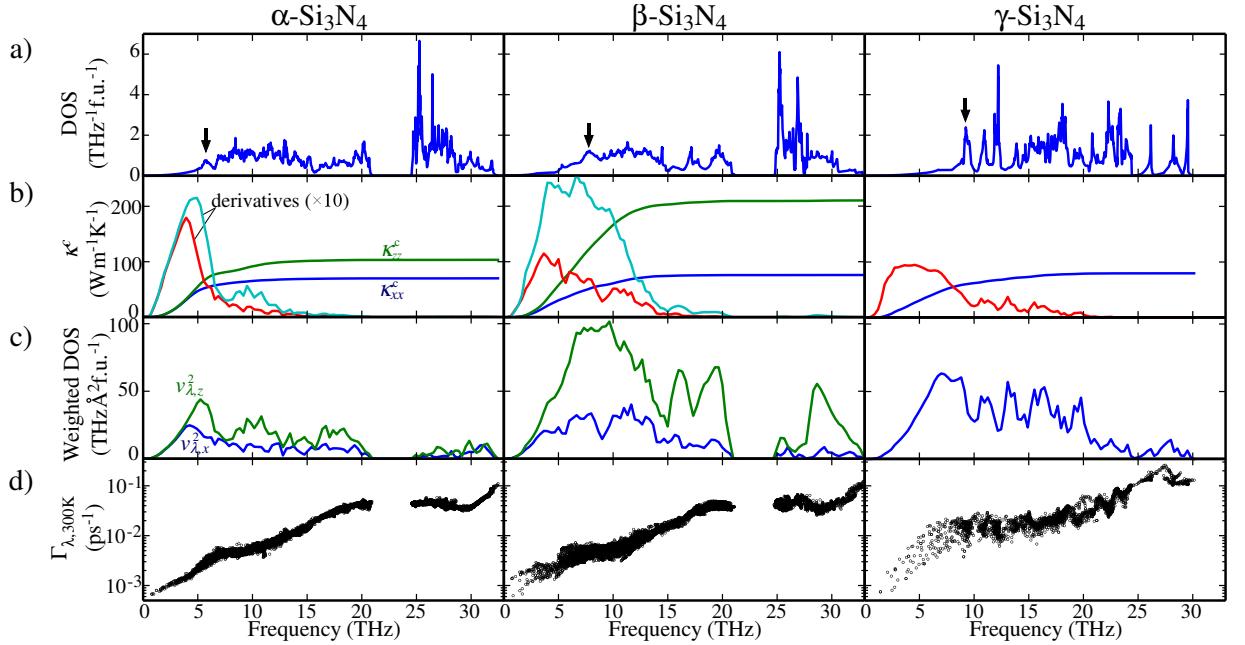


FIG. 5. (color online) Microscopic phonon properties of three  $\text{Si}_3\text{N}_4$  phases. Cumulative thermal conductivity  $\kappa^c$  and its derivative (a), DOS (b), weighted DOS with  $v_{\lambda,i}^2$  (c) and linewidth  $\Gamma_\lambda$  (d).

weighted DOS of  $v_{\lambda,z}^2$  in  $\beta\text{-Si}_3\text{N}_4$  critically causes the large anisotropy in its LTCs.

Fig. 5-d shows significantly similar linewidth distributions between the  $\alpha$  and  $\beta$  phases, which let the group velocities alone play the critical role on the different degrees of the anisotropy in the LTCs. Since it is curious that the linewidths are similar between these phases although their group velocities have marked differences, we investigate this similarity further. Previously, Lindsay *et al.* have pointed out a significant positive correlation between LTC and phase space available for the three-phonon scattering according to the selection rules due to the momentum and energy conservation for the three-phonon processes.<sup>40</sup> More recently Togo *et al.* have shown that the frequency profiles of the imaginary part of self-energy  $\Gamma_\lambda(\omega)$ , where  $\Gamma_\lambda(\omega_\lambda) = \Gamma_\lambda$ , are characterized by the three phonon selection rules.<sup>15</sup> In Eq. (1) of the linewidths,  $\Phi_{-\lambda\lambda'\lambda''}$  partly contains the selection rule due to the momentum conservation.<sup>41</sup> In the present study, we examine the impacts on the linewidths of  $\Phi_{-\lambda\lambda'\lambda''}$  and the whole selection rules, one by one.

In Table. III, the magnitudes of  $\Phi_{-\lambda\lambda'\lambda''}$  are compared as the averages over the  $\omega_\lambda$  frequency ranges between 0–15 and 0–35 THz and over all  $\lambda'$  and  $\lambda''$ . The values of the  $\alpha$  and  $\beta$  phases are very close to each other, indicating that  $\Phi_{-\lambda\lambda'\lambda''}$  have similar impacts.

In order to analyze the impacts of the selection rules on the linewidths, we employ the joint density of states (JDOS)  $D_2(\mathbf{q}, \omega)$ ,

$$D_2(\mathbf{q}, \omega) = D_2^{(1)}(\mathbf{q}, \omega) + D_2^{(2)}(\mathbf{q}, \omega) \quad (4)$$

TABLE III. Averages of  $\Phi_{-\lambda\lambda'\lambda''}$  over frequency ranges of  $\omega_\lambda$  (0–15 and 0–35 THz) and all  $(\lambda', \lambda'')$ . The values are in units of  $10^{-10} \text{ eV}^2 \text{f.u.}^{-1}$ .

Frequency Range (THz)	Phase		
	$\alpha$	$\beta$	$\gamma$
0–15	2.66	2.63	5.76
0–30	13.1	13.0	11.4

where

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

with  $\Delta(\mathbf{x})$  giving 1 if  $\mathbf{x}$  is a reciprocal lattice vector and otherwise zero.

Fig. 6 shows the frequency-dependences of JDOS at different  $\mathbf{q}$ -points on the  $\Gamma\text{-A}$  and  $\Gamma\text{-K}$  paths, which show very slight  $\mathbf{q}$ -point dependence. Eq. (1) includes Bose-Einstein functions for the involved phonon modes and JDOS can be weighted with them as done in refs. 15 and 38, however we omit them for simplicity. With the weights, the absolute values are affected but the weighted JDOS of the  $\alpha$  and  $\beta$  phases are still similar. At the low frequency region responsible for the LTCs, among the two terms of  $D_2^{(1)}$  and  $D_2^{(2)}$  in Eq. (4), dominant is

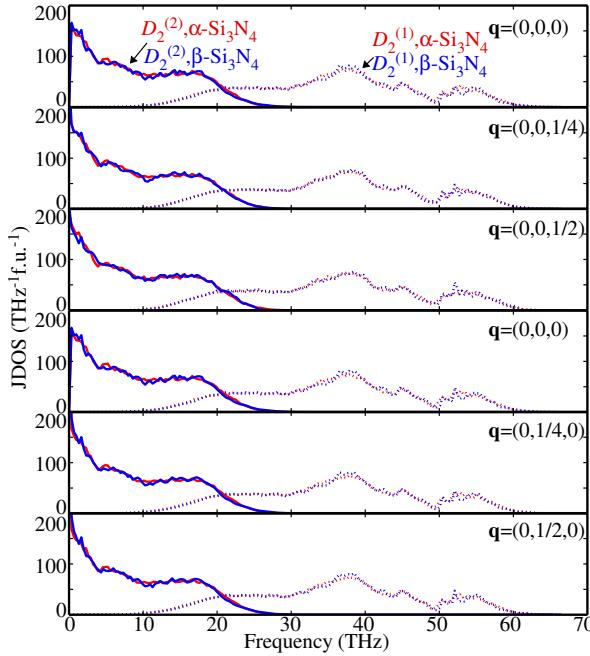


FIG. 6. (color online) JDOS of  $\alpha$ - and  $\gamma$ - $\text{Si}_3\text{N}_4$  at different  $\mathbf{q}$  points. The first and forth rows are JDOS at the same  $\Gamma$ -point but calculated with the polarization for non-analytic term correction set along  $c^*$  and  $b^*$ , respectively.

$D_2^{(2)}$  which basically corresponds to the half part ( $\omega \geq 0$ ) of the auto-correlation function of DOS, which, for the  $\alpha$  and  $\beta$  phases, commonly show the frequency gap (Fig. 5-a).  $D_2^{(2)}$  curves reflect this DOS feature, dropping suddenly around 0 THz and showing a small shoulder around 5 THz, which corresponds to the width of the gap. Moreover  $D_2^{(2)}$  shows a broad peak around 18 THz, which corresponds to the frequency shift to make the largest correlation between the higher and lower portions of DOS across the gap. Because the gap is basically originated from the differences in the vibrations of the planer  $\text{NSi}_3$  commonly contained in the  $\alpha$  and  $\beta$  phases<sup>39</sup>, the major shapes of  $D_2^{(2)}$ , reflecting this gap feature, are similar in these phases. With the same origin, the JDOS of  $D_2^{(1)}$  are also similar in these phases. With these similar impacts of  $\Phi_{-\lambda\lambda'\lambda''}$  and JDOS on  $\Gamma_\lambda$ ,  $\Gamma_\lambda$  in Fig. 5-d are similar.

As a small but interesting difference in the linewidths between these phases,  $\Gamma_\lambda$  below 5 THz in Fig. 5-d are aligned on a smooth line in the  $\alpha$  phase, while those in the  $\beta$  phase are scattered roughly onto two different lines. This difference can be explained by the vibration directions shown in Fig. 7. In Fig. 7-a,  $\Gamma_\lambda$  are classified using colors according to the sums of the squares of the eigenvector components along  $\mathbf{q}$ ; the sum is 1 for perfectly longitudinal waves. However, these sums have no clear contrast to distinguish the two branches in the  $\beta$  phase. Fig. 7-b shows the same plot as Fig. 7-a, but with colors according to the sums of the squares of the eigenvector components along the  $a$ - $b$  plane, which has 1 when the

eigenvectors lie on the  $a$ - $b$  plane. There is a tendency in the  $\beta$  phase that  $\Gamma_\lambda$  are large for the vibrations along the  $a$ - $b$  plane. Therefore, within the single-mode RTA, for the phonon modes below 5 THz, all of which belong to the acoustic phonon branches, the vibration modes along the  $a$ - $b$  plane are more easily scattered in the  $\beta$  phase, no matter whether they are longitudinal or transverse. For the panel of  $\beta$ - $\text{Si}_3\text{N}_4$  in Fig. 7-b, a straight line can divide the phonon modes into the two groups. The numbers of the phonon modes in the upper and lower parts are 157 and 58, whose ratio is rational as the population ratio of the vibration modes along and out of the  $a$ - $b$  plane.

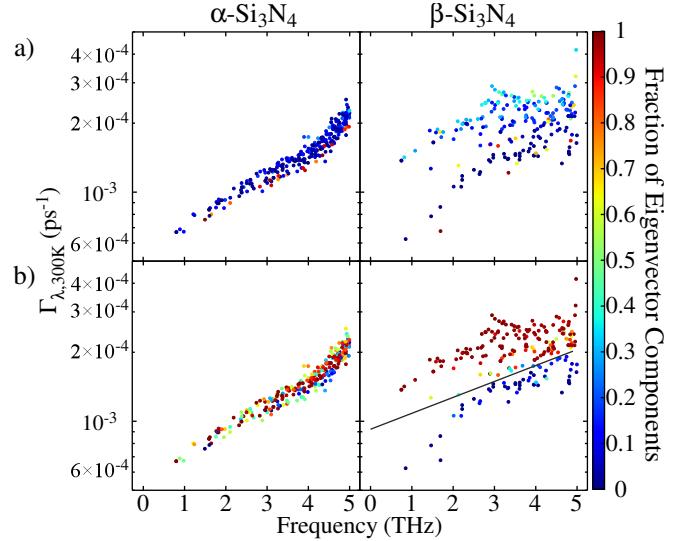


FIG. 7. (color online) Distribution of linewidths  $\omega_\lambda \leq 5$  THz with colormaps with respect to strengths of eigenvector components along  $\mathbf{q}$  (a) and on  $a$ - $b$  plane (b).

#### IV. SUMMARY

In the present study, we investigate the lattice thermal conductivities of the three  $\text{Si}_3\text{N}_4$  phases, by using the lattice dynamics based on the *ab-initio* interatomic force constants. The main remarks are as follows:

1) In the  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$ , whose crystal structures are characterized by the stacking manners of the basal layers, which alter the LTCs. In  $\alpha$ - $\text{Si}_3\text{N}_4$ , the LTC tensors are rather isotropic, while  $\kappa_{zz}$  of the  $\beta$  phase is much larger than the others, showing remarkable anisotropy in the LTC tensor.

2) In the  $\alpha$  phase, the acoustic mode phonons below 6 THz are the main heat carriers, while in the  $\beta$  phase, the phonons below 12 THz contribute to the thermal conductivity. Their group velocities are significantly different between the phases; their linewidths are basically similar due to the similar impacts of the phonon-phonon interaction strengths and selection rules. Therefore the difference in the group velocities alone qualitatively explains the difference of anisotropy.

3) In the  $\gamma$  phase, the frequency distribution of the phonon mode contributions to LTC is found to be similar to that for  $\kappa_{xx}$  of  $\beta\text{-Si}_3\text{N}_4$  although the respective phonon properties (group velocities and linewidths) are much different from those of the other phases

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## Appendix A: Pressure dependence of LTC of $\gamma$ -phase

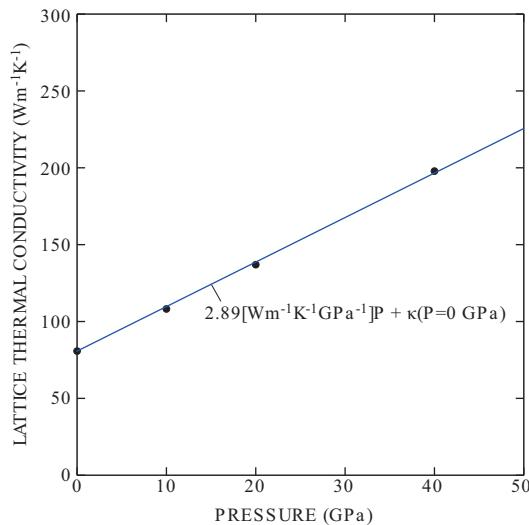


FIG. 8. (color online) Pressure dependence of LTC of  $\gamma\text{-Si}_3\text{N}_4$ .

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