

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

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Lattice thermal conductivities of α -, β - and γ - Si_3N_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 α - Si_3N_4 is calculated as $\kappa_{xx} = 69$ and $\kappa_{zz} = 99$ (in units of $\text{Wm}^{-1}\text{K}^{-1}$). For β - Si_3N_4 , $\kappa_{xx} = 73$ and $\kappa_{zz} = 198$ are obtained, that is consistent with the reported experimental values of 69 and 180, respectively. The difference of anisotropy between α - Si_3N_4 and β - Si_3N_4 is originated from their characteristic difference in the phonon band structures, although their crystal structures are similar in their local atomic coordinates. In α - Si_3N_4 , acoustic-mode phonons below 6 THz are the main heat carriers. In β - Si_3N_4 , the phonon modes up to 12 THz contribute to the lattice thermal conductivity. In γ - Si_3N_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 κ_{xx} of β - Si_3N_4 although the phonon lifetimes of γ - Si_3N_4 are twice shorter than those of β - Si_3N_4 .

I. INTRODUCTION

Several nitride insulators exhibiting high thermal conductivities are important for heat sink materials used at elevated temperatures. Wurtzite-type w-AlN, which has an Adamantine (diamond-like) crystal structure, was noted by Slack *et al.*¹ as a superior thermal conductor over 100 $\text{Wm}^{-1}\text{K}^{-1}$. Si_3N_4 has been more recently recognized as one of the good thermally conductive insulators. Remarkable advances in ceramic technologies related to the densification of the sintered body and microstructural control have pushed the thermal conductivities of polycrystalline of Si_3N_4 ceramics up to 177 $\text{Wm}^{-1}\text{K}^{-1}$.²⁻⁵ Since Si_3N_4 ceramics also exhibit high mechanical strength at elevated temperatures, 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 exists in one of two phases, α and β , both in the hexagonal lattice system, which are generally considered to be low- and high-temperature phases, respectively.^{2,5,6} Their crystal structures are commonly formed by stacking of basal layers of SiN_4 tetrahedra. The stacking manners in α and β - Si_3N_4 are as ABCDABCD.. and ABAB.., respectively. This difference is depicted in Fig. 1 from the principal axis direction. The CD layers are related to AB by the c glide operation,⁷ along which the unit cell periodicity of the α phase is approximately two times longer than that of the β phase, with lattice constants of $c = 5.62 \text{ \AA}^8$ and 2.91 \AA^9 , respectively. In addition to these phases, a cubic spinel phase (γ - Si_3N_4) can be formed upon compression and in-situ heating.^{10,11} The reported transition pressures were scattered from 10 to 36 GPa depending on the experimental conditions.¹² The produced γ phase

can be experimentally quenched to atmospheric pressure and room temperature.

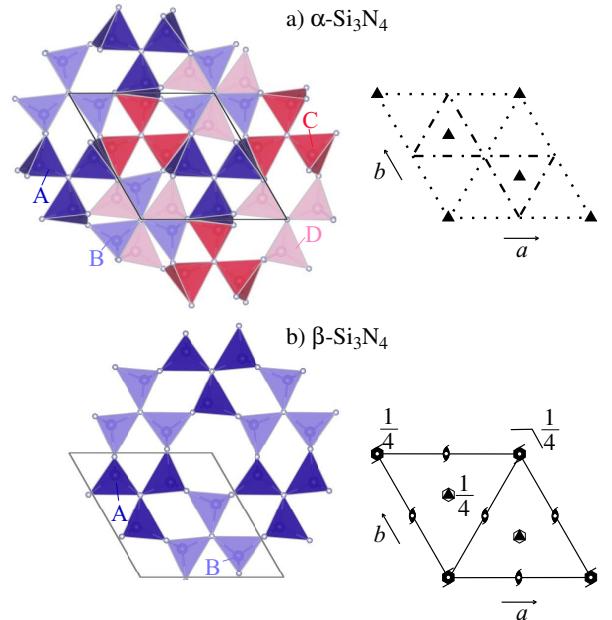


FIG. 1. (color online) Crystal structures of α - and β - Si_3N_4 . Stacking of SiN_4 tetrahedron layers are shown in left. (a) ABCDABCD.. for α - Si_3N_4 . (b) ABAB.. for β - Si_3N_4 . Space group diagrams¹³ in $P31c$ (α - Si_3N_4) and $P63/m$ (β - Si_3N_4) are shown in right.

By using high-resolution thermoreflectance microscopy, Li *et al.*¹⁴ reported that the thermal conductivities of individual rod-shaped β - Si_3N_4 grains in a ceramic were 69 and $180 \text{ Wm}^{-1}\text{K}^{-1}$ along the a and c axes, respectively, and thus suggested its large

anisotropy in thermal conductivity. Takahashi *et al.*¹⁵ have recently developed a technique by which $\beta\text{-Si}_3\text{N}_4$ grains are coated with graphene of relatively high magnetic susceptibility, enabling them to align their c axis along the external magnetic field. Based on this technique, it has been proposed that the textural structure of rod-shaped $\beta\text{-Si}_3\text{N}_4$ grains would increase their thermal conductivity to a level matching or exceeding that of w-AlN.

Although the fabrication of millimeter-sized $\beta\text{-Si}_3\text{N}_4$ single crystals has been reported,¹⁶ the thermal conductivity of an isolated single crystal of any Si_3N_4 phase has not yet been experimentally determined. It was proposed that the anisotropy in the thermal conductivity of $\beta\text{-Si}_3\text{N}_4$ phase grains may not stem from the intrinsic crystal properties, but rather, from the selective removal of crystal defects along the c axis of the grains.¹⁷ Theoretically, Hirosaki *et al.*¹⁸ estimated the room-temperature lattice thermal conductivities (LTCs) κ_{xx} and κ_{zz} of $\alpha\text{-Si}_3\text{N}_4$ to be 105 and $225 \text{ W m}^{-1}\text{K}^{-1}$, and those of $\beta\text{-Si}_3\text{N}_4$ to be 170 and $450 \text{ W m}^{-1}\text{K}^{-1}$, respectively, by applying the Green-Kubo formulation to the molecular dynamics (MD) method with the interatomic potentials proposed by Vashishta *et al.*¹⁹ Although the absolute values were more than two times larger, the ratio of the LTCs in the β phase along the a and c axes agreed well with the experimental results obtained by Li *et al.*¹⁴ Moreover, the MD results suggest that the different stacking orders between α - and $\beta\text{-Si}_3\text{N}_4$ alter their LTC largely. On the other hand, the recent LTC calculation based on first principles calculation and Boltzmann transport theory has shown that in many polymorphs of the wurtzite and zincblende structures, which have different stacking orders of the densest atom planes as ABAB.. and ABCABC.., these orders merely alter the LTCs.²⁰ **It is interesting to investigate it using this approach for α - and $\beta\text{-Si}_3\text{N}_4$.**

In addition to these phases, a cubic spinel phase ($\gamma\text{-Si}_3\text{N}_4$) can be formed upon compression and in-situ heating.^{10,11} The reported transition pressures were scattered from 10 to 36 GPa depending on the experimental conditions. The produced γ phase can be experimentally quenched to atmospheric pressure and room temperature. Its thermal conductivity has not been experimentally reported; it has been estimated only by the Slack model.²¹

The present study aims to qualitatively understand the LTC tensors among the three Si_3N_4 phases by means of the first principles approach. After the methodology section, we examine the validity of the present LTC results first. Then we investigate the characteristics in the LTCs in detail.

II. COMPUTATIONAL PROCEDURES

A. Lattice thermal conductivity calculation

The LTCs were calculated by solving the linearized Boltzmann transport equation (LBTE) within the single-mode relaxation time approximation (single-mode RTA). We also tried the direct-solution of LBTE²² and leave its calculated LTC values in the following section. The difference of LTCs 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 LTCs.

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, $\tau_{\lambda, \text{ph-ph}} = (2\Gamma_{\lambda})^{-1}$, 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 ω_{λ} is the harmonic phonon frequency of the phonon mode λ , $n_{\lambda} = [\exp(\hbar\omega_{\lambda}/k_B T) - 1]^{-1}$ 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 IFCs from direct space to phonon space.²⁰ The second- and third-order real-space IFCs 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 LTC 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.²³ With the relaxation times of the phonon-phonon scattering and isotopic scattering, $\tau_{\lambda, \text{ph-ph}}$ and $\tau_{\lambda, \text{iso}}$, the total relaxation time for a phonon mode was assumed to be $1/\tau_{\lambda} = 1/\tau_{\lambda, \text{ph-ph}} + 1/\tau_{\lambda, \text{iso}}$, according to Matthiessen's rule.

These LTCs were calculated with the phonon-phonon interaction calculation code PHONO3PY,²⁰ while the harmonic phonon states were analyzed with the phonon calculation code PHONOPY.²⁴

The available experimental thermal conductivity data of the Si_3N_4 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 $\tau_{\lambda, \text{bs}} = L/|\mathbf{v}_{\lambda}|$ of a phonon boundary scattering model, where $\mathbf{v}_{\lambda} = \nabla_{\mathbf{q}}\omega_{\lambda}$ is the group velocity and L a parameter regarding to

the boundary mean free path. We consider $\tau_{\lambda,bs}$ as a variable parameter and included it to LTCs according to Matthiessen's rule.

The closed form of the LTC tensors within RTA were 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 the LTC in detail, we calculate the cumulative thermal conductivity:

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

B. Computational details

The IFCs were calculated using the first-principles projector augmented wave method²⁵ (VASP code^{26–28}). The generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof²⁹ was used for the exchange correlation potential. A plane wave energy cut-off of 500 eV was employed. The crystal structures were optimized until the convergence in 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 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 agree with the experimental data^{8,9,30} within +0.7 % errors. The lattice volume optimized at 0 K and 0 GPa within the local density approximation (LDA)³¹ for the exchange correlation potential was, for $\beta\text{-Si}_3\text{N}_4$, 3 % smaller than the volume with GGA, which is a typical volume contraction of LDA. In our test using $\beta\text{-Si}_3\text{N}_4$ at 0 K and 0 GPa, the LTC calculated with LDA was larger by 2.6 % than that with GGA. For our discussion, these 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 IFCs.³² The $1 \times 1 \times 2$, $1 \times 1 \times 3$, and $1 \times 1 \times 1$ supercells of the conventional unit cells were adopted for the third-order IFCs of the α , β , and γ phases, respectively, while the larger supercells $3 \times 3 \times 4$, $3 \times 3 \times 8$ and $2 \times 2 \times 2$ were adopted for the respective second-order IFCs. The constant atomic displacement distance was set to 0.03 Å. Table I shows the calculated LTC values for several different choices of supercell sizes, indicating that our calculated LTCs are reasonably converging with respect to the supercell sizes.

TABLE I. Calculated lattice thermal conductivities (LTC) of α -, β -, 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 rd FC	2 nd FC	<i>xx</i>	<i>zz</i>
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)	56	81
	1 \times 1 \times 2 (56)	2 \times 2 \times 2 (224)	70	98
	1 \times 1 \times 2 (56)	2 \times 2 \times 3 (336)	69	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)	40	166
	1 \times 1 \times 2 (28)	2 \times 2 \times 4 (224)	75	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	197
	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

Non-analytical term correction³³ was applied to the second-order IFC to take into account the long range Coulomb forces present in ionic crystals. For the correction, Born effective charges were calculated by using the present band method.

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 IFCs of the α , β , and γ phases. For the former two phases the center of the $a^* \text{-} b^*$ plane were sampled though the off-center grids along c^* -axis were sampled. For the γ phase, non- Γ center mesh was used. For the second-order IFC, the Γ -point was only sampled for the α and β phase supercells and the only one $\mathbf{k} = (0.5, 0.5, 0.5)$ point was sampled for the γ phase supercell. 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 the LTCs in Eq. (2) for the α , β , and γ phases.

To compare the calculated LTC with the experimental data measured at finite temperatures, the experimentally measured lattice parameters may be preferred in case that they are known. We examined LTC of $\beta\text{-Si}_3\text{N}_4$ at the equilibrium volumes ($V_{\text{eq}}(T)$) within the quasi-harmonic approximation (QHA).³⁴ Except for this, the LTC values were calculated with the equilibrium volume at 0 K ($V_{\text{eq}}(T = 0)$).

We calculated volumetric thermal expansion coefficients and compared them with the reported experimental values so as to check the validity of the present calculation, because the thermal expansion is originated from the anharmonicity of the interatomic potential as well as lattice thermal conduction. The calculated values are 4.31 and 4.19 (10^{-6} K^{-1}) at 300 K for the α and β phases, while the experimental values were 3.75 and 3.55 (10^{-6} K^{-1})³⁵. The present calculation reproduced the experimental tendency where the α phase has a slightly larger

thermal expansion coefficient than the β phase, supporting that the present calculations enable us to qualitatively compare the LTC values of the Si_3N_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 γ phase, this means that we assume the condition of virtually quenched γ phase at 0 GPa from the high pressure. To examine this, we calculated LTC of γ phase at 10, 20, and 40 GPa as shown in Fig. 8, where the phenomenological behaviour of linear dependence of LTC 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. 36. By this result, we consider that the microscopic values are also varied smoothly with the pressure and those at 0 GPa are meaningful to compare with the α and β phases.

C. Direct solution of LBTE

The merit of the single-mode RTA is that we can intuitively understand the qualitative character of LTC in terms of the relaxation time and group velocity. The microscopic understanding of the full solution of LBTE is still under the development³⁷ and the microscopic picture based on collective phonons³⁸ will require more complicated investigation although it is known that the single-mode RTA solution of LBTE underestimates the full solution.^{39,40}

For the α and β phases, we partly adopted a direct solution of LBTE²², which is one of the methods of LBTE full solutions. The LTC values of the direct solution without the isotope effect were 69 and $102 \text{ Wm}^{-1}\text{K}^{-1}$ for κ_{xx} and κ_{zz} of the α phase and 76 and $238 \text{ Wm}^{-1}\text{K}^{-1}$ for those of the β phase, respectively, while the corresponding single-mode RTA values were 70 and $102 \text{ Wm}^{-1}\text{K}^{-1}$ for the α phase and 76 and $210 \text{ Wm}^{-1}\text{K}^{-1}$ for the β phase. The κ_{zz} of the direct solution in the β phase was 13% larger than that of the single-mode RTA solution. Since the LTC difference between the LBTE solutions is not significant, we expect the physics on LTC is well understood within RTA in the current level of our interest.

III. RESULTS AND DISCUSSION

A. Lattice thermal conductivities

In Table II, the theoretical LTCs at 300 K are compared with the previously reported experimental^{5,14,41,42} and theoretical^{18,20,21} values. The present calculation results better agree with the experimental κ_{xx} and κ_{zz} of $\beta\text{-Si}_3\text{N}_4$, compared with the references of the Slack model²¹ and MD¹⁸ results. The directional averages of the present κ_{ii} in the α , β , and γ phases are 79 , 115 , and $81 \text{ Wm}^{-1}\text{K}^{-1}$. The value of the γ phase is just as small as that of the α phase, although the former phase shows the largest bulk modulus (B) in Table II. It is generally

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			Ref. Theo.			Ref. Expt.		
	κ_{xx}	κ_{zz}	B	κ	κ_{xx}	κ_{zz}	κ	κ_{xx}	κ_{zz}
$\alpha\text{-Si}_3\text{N}_4$	68	100	224	70 ^a	105 ^b	225 ^b	59 ^d	-	-
$\beta\text{-Si}_3\text{N}_4$	73	199	237	250 ^a	170 ^b	450 ^b	122 ^e	69 ^f	180 ^f
$\gamma\text{-Si}_3\text{N}_4$	77	-	296	80 ^a	-	-	-	-	-

^a Ref. 21, Slack model.

^b Ref. 18, molecular dynamics (Green-Kubo).

^c Ref. 41, thin film.

^d Ref. 5, poly-crystals.

^e Ref. 14, single crystalline grains of poly-crystals.

known that simple models through Debye temperature can provide only their rough estimations.

It can be seen that the theoretical LTCs of $\beta\text{-Si}_3\text{N}_4$ are markedly more anisotropic than those of the α phase. The theoretical LTCs of $\beta\text{-Si}_3\text{N}_4$ are in good agreement with the corresponding experimental data for individual grains reported by Li *et al.*¹⁴, indicating that the experimentally reported large anisotropy in the thermal conductivities of $\beta\text{-Si}_3\text{N}_4$ stems from the intrinsic properties of the crystal, rather than specific defects induced during the sample preparation process.

Fig. 2 shows the theoretical LTCs of the α and β phases as a function of T , in comparison with the reference experimental data, which were measured from the polycrystalline samples. The data of the polycrystalline bulk samples cannot be directly compared with the theoretical LTC tensors because the microstructures of the bulk samples affect the thermal conductivities. We calculate theoretical LTC values of the polycrystalline bulk sample as $\kappa = w\kappa_{xx} + (1-w)\kappa_{zz}$, with an adjustable parameter w between 0 and 1 for the least square differences from the experimental data.

The temperature dependence of the theoretical LTC, induced by $\tau_{\lambda,\text{ph-ph}}$, is close to T^{-1} because 300 K is high enough to approximate the linewidth in Eq. (1) by a high-temperature limit for these phases. In Fig. 2-a, the temperature dependence of the experimental data of a chemically vapor-deposited $\alpha\text{-Si}_3\text{N}_4$ sample⁴¹ is deviated from T^{-1} considerably, intersecting the theoretical curves of the κ_{xx} and κ_{zz} . Thus no value of w adjusts the theoretical LTC to the experimental curve. 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 according to Matthiessen's rule, could not explain the discrepancy as well. $\tau_{\lambda,\text{bs}} = L/|\mathbf{v}_{\lambda}|$ with $L = 0.75 \mu\text{m}$, which was much smaller than the experimental grain size $10 \mu\text{m}$, decreases the room-temperature theoretical κ_{xx} and κ_{zz} values toward the experimental values, but severely underestimated the experimental values at the high tem-

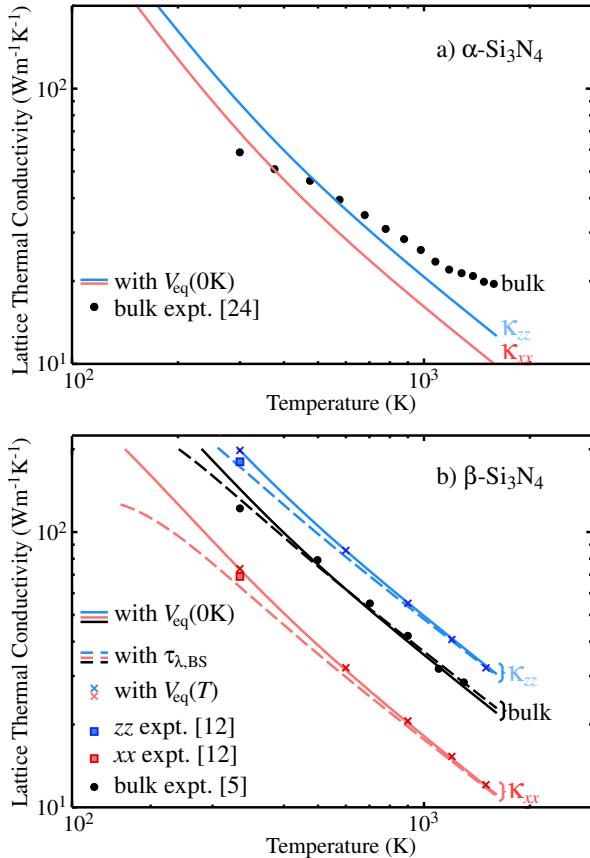


FIG. 2. (color online) Temperature dependence of LTC for α - and β - Si_3N_4 . The LTC calculated with the fixed volume optimized at 0 K are shown by the solid curves. For β - Si_3N_4 , the LTC with the boundary scattering effect are shown by broken curves. The LTC calculated with the equilibrium volumes at the temperatures are shown by crosses. Theoretical LTC for the bulk β - Si_3N_4 sample are also shown to be compared with the experimental LTC (filled circles) of the bulk sample.

perature 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 α - Si_3N_4 , significant lattice defects might exist in the as-deposited sample as pointed out by Hirosaki *et al.*¹⁸ and the simple phonon boundary scattering model might fail to describe their effects. The experimental values of the β phase ceramic bulk⁵ in Fig. 2-b fall well between the calculated values of κ_{xx} and κ_{zz} , being nearly parallel to the theoretical κ_{xx} and κ_{zz} curves. If we compare the experimental values with $\sum_i \kappa_{ii}/3$, which is a simple directional average, the calculation shows slight underestimations with respect to the experiment, which can be understood from an experimentally tailored microstructure containing large β - Si_3N_4 grains selectively grown along the c axis.⁵

The theoretical curve adjusted with $w = 0.37$ explains well the experimental data of the poly-crystal bulk in Fig. 2-b. For the effects of lattice defects most of which

are grain boundaries, we included $\tau_{\lambda,BS}$ with $L = 1 \mu\text{m}$ to further fit the theoretical curve ($w = 0.44$) to the experimental data. The L value is similar to the average grain size ($2 \mu\text{m}$)⁵ of the experimental polycrystalline sample. Fig. 2-b also contains the experimental κ_{xx} and κ_{zz} at room temperature by filled squares, which are in-between the theoretical components with and without $\tau_{\lambda,BS}$. The LTC values with the equilibrium lattice volumes (V_{eq}) at 300, 600, 900, 1200 and 1500 K within QHA are plotted by crosses in Fig. 2-b. The deviations due to the thermal expansions were less than 1 %. Therefore this effect is negligible for the present study. The degree of the differences is similar to the case of Si and Ge⁴⁰.

B. Dispersion curves

Figure 3 shows the phonon band diagrams of the three Si_3N_4 phases. The entire band diagrams are almost identical to those reported earlier^{12,43}. However, here we focus on the group velocities on high-symmetry paths for the entire frequency range. This has not been investigated by the previous works.

The acoustic branches in the α phase highlighted in red in Fig. 3-a do not increase their frequencies much more than those along the other paths, Γ -K or Γ -M. The frequency maxima along the Γ -A path are around 7 THz, rather close to the maxima along the Γ -K and Γ -M paths (around 5 THz). The upper branches along the Γ -A path are also as flat as the upper branches along the Γ -K and Γ -M paths. In contrast, in the band diagram of the β phase (Fig. 3-b), the acoustic phonon branches highlighted in red along the Γ -A path increase their frequencies almost linearly from the Γ -point to the A-point and reach around 10 THz, along which the group velocity component $v_{\lambda,z}$ maintains high values. This difference is because the Γ -A path length of the β phase is approximately twice that of α ; the lattice constant c of β is nearly half that of α , owing to the difference in the stacking manner of the basal layers. Normally, optical branches are flat; however, the upper branches along the Γ -A path also have significantly large $v_{\lambda,z}$. In Fig. 3-c for the γ phase, the acoustic phonon branches highlighted in red show significant linear dispersions. The frequencies of the longitudinal acoustic modes are 14 and 12.5 THz at the L- and X-points. The frequencies of the transverse acoustic modes are approximately half the values of the longitudinal modes at the L-point and a factor of $1/\sqrt{2}$ smaller than the longitudinal modes at the X-point, as in the case of fcc rare gas solids⁴⁴. The roughly constant gradients of the branches are large, reflecting the large elastic constants of the γ phase as shown in Table II.

C. ω_{λ} counter map on reciprocal plane

In another point of view on the group velocities, Fig. 4 shows the cross-sections of the phonon frequency distri-

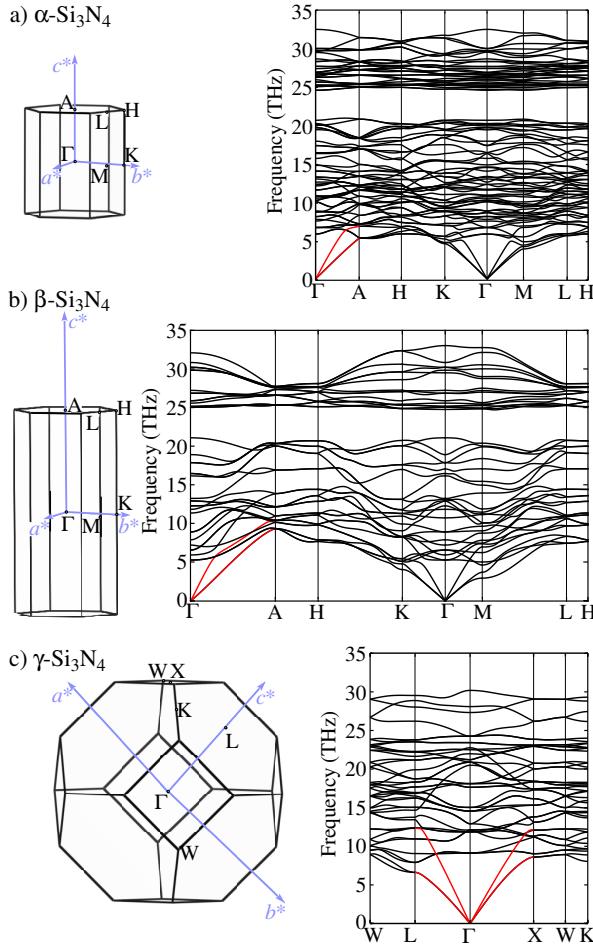


FIG. 3. (color online) Brillouin-zones (left) and calculated phonon band diagrams (right) for three Si_3N_4 phases.

butions on the b^*-c^* planes in the first Brillouin-zones. The cross-sections of other planes containing the c^* axis did not differ much from Fig. 4; thus, we focus on the results for the b^*-c^* planes as representative of all such planes. We show only the frequencies of four modes from the lowest frequency because they contribute significantly to LTC. Fig. 4-a shows that the frequency distributions and group velocities of $\alpha\text{-Si}_3\text{N}_4$ are fairly isotropic. On the other hand, in Fig. 4-b of the β 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 β phase, in a significantly large part of the Brillouin zone, have group velocities oriented along the c axis.

D. Frequency-dependences of κ^c , v_λ and Γ_λ

The microscopic phonon properties we have seen in the previous sections are located in specific paths or planes in the Brillouin zone. In order to more rigorously inspect the LTCs, we examine phonon properties taken over the Brillouin zone. As such properties, in Fig. 5 are shown

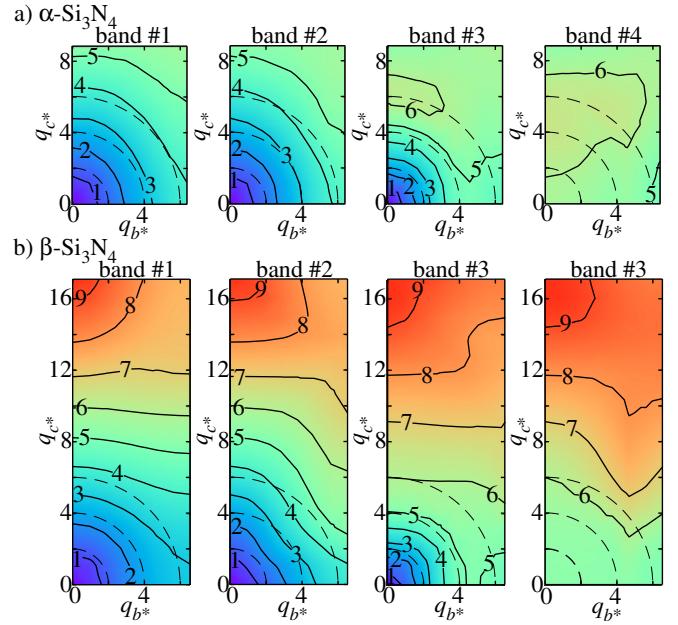


FIG. 4. (color online) Contour maps of phonon frequency (THz) on the b^*-c^* planes of Brillouin-zones. The maps for the four lowest-frequency phonon states are shown. The frequency landscapes are formed by simply connecting the frequencies of the same band indices, assigned by ascending order of frequency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

phonon densities of states (DOS), cumulative thermal conductivities and their frequency derivatives, weighted DOS with the squares of the group velocity components ($v_{\lambda,x}$ and $v_{\lambda,z}$), and finally, frequency distributions of linewidths.

Firstly, we relate DOS (Fig. 5-a) with the cumulative thermal conductivity κ^c (Fig. 5-b). The first DOS peaks indicated by arrows are related to the flattening of the acoustic branches at the Brillouin zone boundaries. As κ^c increasing up to around 6, 12 and 10 THz for the α , β and γ phases, the phonons contributing to the LTCs are mainly located on the frequencies below the first peaks except for the β phase, where almost a half of the contributions to the LTCs are derived from the phonons above the first peak, indicating that the low frequency optical phonons should contribute to these components significantly. Therefore κ^c in the γ phase resembles closely to κ_{xx}^c in the β phase, but the respective phonon properties are much different. In the frequency range responsible for the LTC, the weighted DOS in the γ phase exceeds that with $v_{\lambda,x}^2$ in the β phase, while the linewidths are twice larger.

In Figs. 5-b and c, the directional differences in the derivatives of κ_{ii}^c in the α and β phases are qualitatively well consistent with the directional differences in the weighted DOS. The relatively larger intensities in the 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 distribu-

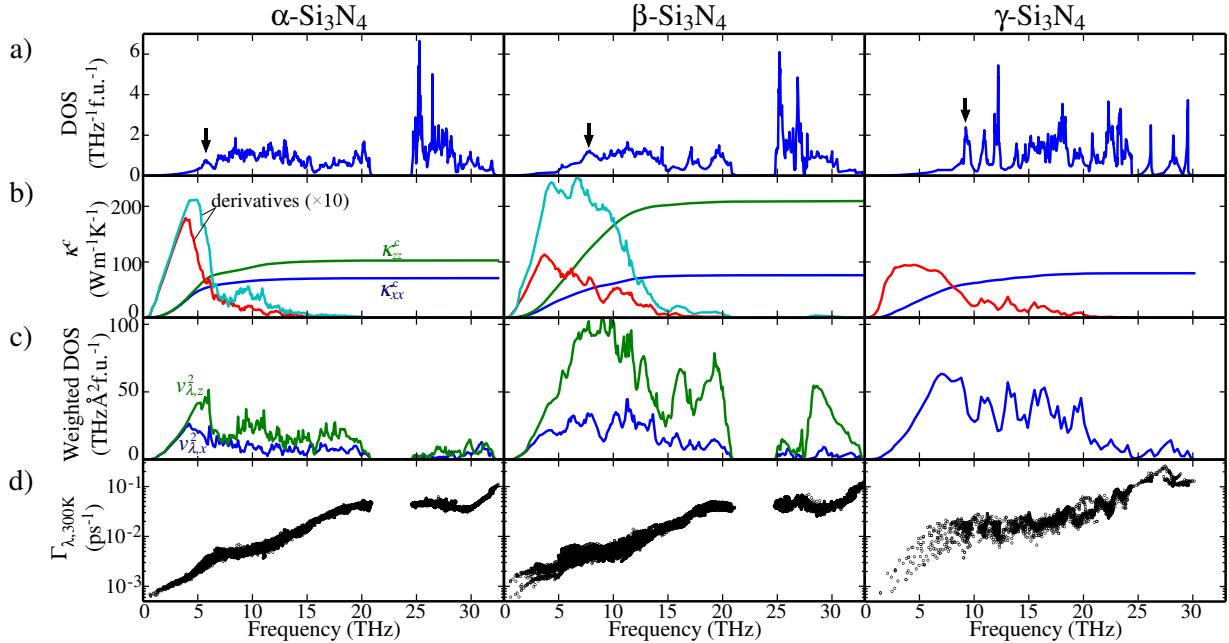


FIG. 5. (color online) Microscopic phonon properties of three Si_3N_4 phases. Cumulative thermal conductivity κ^c and its derivative (a), DOS (b), weighted DOS with $v_{\lambda,i}^2$ (c) and linewidth Γ_λ (d).

tions between the α and β 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.⁴⁵ 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.²⁰ In Eq. (1) of the linewidths, $\Phi_{-\lambda\lambda'\lambda''}$ partly contains the selection rule due to the momentum conservation.⁴⁶ 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 ω_λ frequency ranges between 0–15 and 0–35 THz and over all λ' and λ'' . The values of the α and β 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 ω_λ (0–15 and 0–35 THz) and all (λ', λ'') . The values are in units of $10^{-10} \text{ eV}^2 \text{f.u.}^{-1}$.

Frequency Range (THz)	Phase		
	α	β	γ
0–15	2.66	2.62	5.75
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 Γ –A and Γ –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. 20 and 39, however we omit them for simplicity. With the weights, the absolute values are affected but the weighted JDOS of the α and β 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

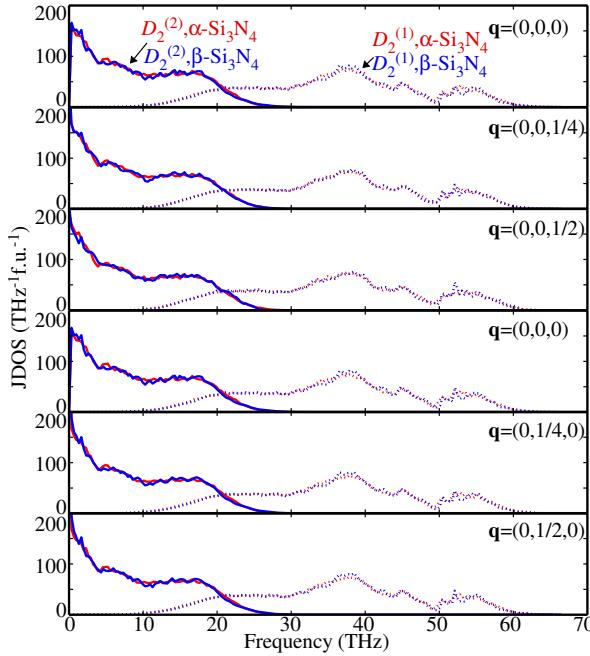


FIG. 6. (color online) JDOS of α - and γ - Si_3N_4 at different \mathbf{q} points. The first and forth rows are JDOS at the same Γ -point but calculated with the polarization for non-analytic term correction set along c^* and b^* , respectively.

$D_2^{(2)}$ which basically corresponds to the half part ($\omega \geq 0$) of the auto-correlation function of DOS, which, for the α and β 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 NSi_3 commonly contained in the α and β phases⁴³, 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 Γ_λ , Γ_λ in Fig. 5-d are similar.

As a small but interesting difference in the linewidths between these phases, Γ_λ below 5 THz in Fig. 5-d are aligned on a smooth line in the α phase, while those in the β 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, Γ_λ 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 β 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 β phase that Γ_λ 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 β phase, no matter whether they are longitudinal or transverse. For the panel of β - Si_3N_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 357 and 126, whose ratio is rational as the population ratio of the vibration modes along and out of the a - b plane.

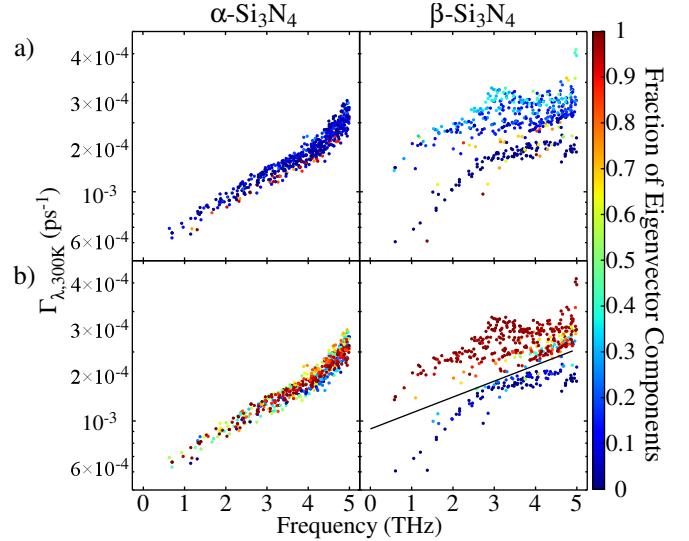


FIG. 7. (color online) Distribution of linewidths $\omega_\lambda \leq 5$ THz with colormaps with respect to strengths of eigenvector components along \mathbf{q} (a) and on a - b plane (b).

IV. SUMMARY

In the present study, we investigate the lattice thermal conductivities of the three Si_3N_4 phases, by using the lattice dynamics based on the *ab-initio* interatomic force constants. The main remarks are as follows:

1) In the α - and β - Si_3N_4 , whose crystal structures are characterized by the stacking manners of the basal layers, which alter the LTCs. In α - Si_3N_4 , the LTC tensors are rather isotropic, while κ_{zz} of the β phase is much larger than the others, showing remarkable anisotropy in the LTC tensor.

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 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 γ phase, the frequency distribution of the phonon mode contributions to LTC is found to be similar to that for κ_{xx} of $\beta\text{-Si}_3\text{N}_4$ but the respective phonon properties are much different: The group velocities in the γ phase are in between the group velocity components along x and z in the β phase, while the phonon scattering lifetimes are twice shorter than those of $\beta\text{-Si}_3\text{N}_4$.

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Appendix A: Pressure dependence of LTC of γ -phase

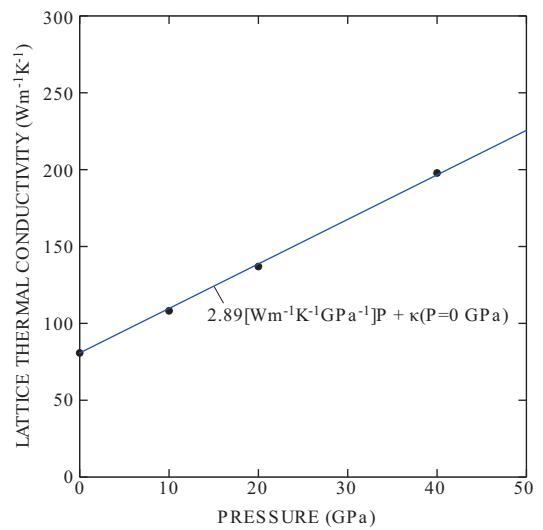


FIG. 8. (color online) Pressure dependence of LTC of $\gamma\text{-Si}_3\text{N}_4$.

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