Pressure-induced phase transition in silicon nitride material*

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The equilibrium crystal structures, lattice parameters, elastic constants, and elastic moduli of the polymorphs α-, β-, and γ-Si_3N_4, have been calculated by first-principles method. β-Si_3N_4 is ductile in nature and has an ionic bonding. γ-Si_3N_4 is found to be a brittle material and has covalent chemical bonds, especially at high pressures. The phase boundary of the $\beta \rightarrow \gamma$ transition is obtained and a positive slope is found. This indicates that at higher temperatures it requires higher pressures to synthesize γ-Si_3N_4. On the other hand, the $\alpha \rightarrow \gamma$ phase boundary can be described as $P = 14.37198 + 3.27 \times 10^{-3}T - 7.83911 \times 10^{-7}T^2 - 3.13552 \times 10^{-10}T^3$. The phase transition from α- to γ-Si_3N_4 occurs at 16.1 GPa and 1700 K. Then, the dependencies of bulk modulus, heat capacity, and thermal expansion on the pressure P are obtained in the ranges of 0 GPa–30 GPa and 0 K–2000 K. Significant features in these properties are observed at high temperatures. It turns out that the thermal expansion of γ-Si_3N_4 is larger than that of α-Si_3N_4 over wide pressure and temperature ranges. The evolutions of the heat capacity with temperature for the Si_3N_4 polymorphs are close to each other, which are important for possible applications of Si_3N_4.

Keywords: density functional theory, semiconductor, heat capacity, bulk modulus

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1. Introduction

Silicon nitride (Si_3N_4) is known to have excellent mechanical strength, low compressibility, high thermal stability, good oxidation resistance, excellent creep resistance, good erosion resistance, low density, and high decomposition temperature.[1] Due to its wide applications in cutting tools, motors, turbines, antifriction bearings, and etch masks in microelectronics, the mechanical and thermal properties of Si_3N_4 (under ambient conditions) have been investigated extensively by both theory and experiment.[2–8] In contrast, its high-temperature and high-pressure properties are less known. There are two well-known phases of silicon nitride, α- and β-Si_3N_4, both have hexagonal structures. Of great interest, a third form of Si_3N_4 with a denser, cubic spinel lattice (γ-Si_3N_4) has been synthesized by the diamond anvil cell technique.[9] The new spinel phase is particularly significant since for the first time Si atoms have been found to have an octahedral coordination in a pure binary material. Upon compression and simultaneous *in situ* heating, both β-Si_3N_4 and α-Si_3N_4 transform into the γ phase, which has been confirmed by experiments.[2,9–11]

Wang *et al.*[12] have investigated the bulk modulus and some thermodynamic properties of α-, β-, and γ-Si_3N_4 using the analytic mean field method. Chen *et al.*[13] have calculated the phonon density of states and heat capacities for β-Si_3N_4 through lattice dynamics. Using the same method, Kuwabara *et al.*[3] have obtained the phonon dispersion curves, phonon DOSs, bulk moduli, thermal expansion coefficients, and heat capacities of α-, β-, and γ-Si_3N_4. Some thermodynamic properties, such as heat capacity, entropy, free energy, phonon DOS, and phonon dispersion curve for α- and β-Si_3N_4, are also given in Refs. [14] and [15]. Nevertheless, in these papers the results are often limited to zero pressure and some fundamental properties are missing. It is found that the transition pressure P_t between β- and γ-Si_3N_4 is approximately 12.5 GPa.[16] Through the X-ray diffraction experiment, Kruger *et al.*[17] have found that α-Si_3N_4 can retain its stability to 48 GPa when compressed statically at 295 K. Kuwabara *et al.*[3] have also calculated the phase transition characters between β- and γ-Si_3N_4 using lattice dynamics ($P_t = 5$ GPa$\sim$7 GPa at $T = 300$ K$\sim$2300 K). Very recently, Xu *et al.*[2] have investigated the $\alpha \rightarrow \gamma$ and $\beta \rightarrow \gamma$ phase transitions for the Si_3N_4 polymorphs. Some thermodynamic properties such as thermal expansion coefficient, bulk modulus, and Grüneisen parameter are also given in Refs. [2] and [3]. The T–P diagrams of the β/γ and α/γ transitions are also clearly shown. In Ref. [2], the transition pressure of the $\alpha \rightarrow \gamma$ transformation is reported to be 8.5 GPa at 1700 K, which is not in agreement with the experimental data ($P_t = 17$ GPa$\pm$0.5 GPa at 1673 K$\sim$1873 K). Therefore, more studies are required to evaluate the transition pressure with higher reliability.

To the best of the authors' knowledge, previous investigations were often concentrated on β-Si_3N_4 and the newly discovered γ phase. Some fundamental properties of α-Si_3N_4 are less known. Due to the difficulties preparing pure α- and γ-Si_3N_4 samples,[18,19] theoretical methods like first-principles

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can help. In this paper, we report a study with two main aims: (i). Highlight the phase diagrams between α-, β-, and γ-Si_3N_4. We try to obtain the phase boundary between β- and γ-Si_3N_4, and, more importantly, the phase boundary between α- and γ-Si_3N_4. (ii). Determine the high-pressure and high-temperature elastic properties, stability, and thermodynamic properties of α-, β-, and γ-Si_3N_4.

2. Calculation methods

Si_3N_4 has three polymorphs, α, β, and γ phases. β-Si_3N_4 (phenacite-type) has a hexagonal structure with two Si_3N_4 molecular units (14 atoms) per unit cell. α-Si_3N_4 (nierite) has a unit cell twice as large and contains twice as many atoms per unit cell. Silicon atoms occupy the 6*c* (1/12, 1/2, 3/4) and 6*c* (1/4, 1/6, 1/2) Wyckoff sites. Nitrogen atoms occupy the 6*c* (2/3, 2/3, 1/2), 6*c* (1/3, 1/3, 3/4), 2*b* (1/3, 2/3, 3/4), and 2*a* (0, 0, 1/2) positions.[20] Space groups $P3_1c$ and $P6_3/m$ are assumed for α- and β-Si_3N_4, respectively.[3,21,22] Different atoms occupy several 6*h* Wyckoff sites, namely N (1/3, 2/3, 1/4), N (0.321, 0.025, 0.25), and Si (0.1740, 0.7659, 0.25) positions.[?] High pressure γ-Si_3N_4 (spinel-type) has a cubic lattice (space group: Fd–$3m$) with 56 atoms in the conventional unit cell. Different atoms occupy the Si-8*a* (1/8, 1/8, 1/8), Si–16*d* (1/2, 1/2, 1/2), and N–32*e* (0.2625, 0.2625, 0.2625) sites.[9] For the Si_3N_4 polymorphs, the α phase is recognized as being metastable relative to the β phase.[17,24,25]

The ground-state structures of Si_3N_4 are optimized in the framework of the first-principles method based on the Kohn–Sham equation.[26] The self-consistent total energy calculations are performed with the plane-wave pseudo-potential (PW-PP) method.[27] The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof[28] is used for the exchange–correlation functional. Convergence tests guided the choice of 500 eV for the cutoff energy, $E_{\rm cut}$. Pseudo-atomic calculations are performed for Si-$3s^2 3p^2$ and N-$2s^2 2p^3$ and the ultrasoft pseudo-potentials are non-local. The *k*-point meshes of the Brillouin zone, based on the Monkhorst–Pack scheme,[29] are 4×4×7 for α-Si_3N_4, 4×4×12 for β-Si_3N_4, and 8×8×8 for γ-Si_3N_4, respectively. All internal coordinates of the atoms have been fully relaxed. Equilibrium structures of the above-mentioned polymorphs are optimized until the total energies are converged to at least 10^{-6} eV/atom. According to the standard thermodynamics, if a system is held at finite temperature and pressure then the free energy G can be expressed as

$$G(V;p,T) = E(V) + PV - TS, \tag{1}$$

where $E(V)$ is the total energy, V the cell volume, and S is the entropy of the system. Since the experimental determination of thermodynamic properties often takes place at finite temperature, the vibrational effects should be considered. So we have chosen the quasi-harmonic Debye (QHD) model[30] and according to this model the non-equilibrium Gibbs free energy $G^*(V;P,T)$ can be written as

$$G^*(V;P,T) = E(V) + PV + A_{\rm vib}(T,\theta_{\rm D}(V)), \tag{2}$$

where PV corresponds to the constant hydrostatic pressure condition. $A_{\rm vib}$ is the vibrational Helmholtz free energy. Series standard thermodynamic relations can be determined by fitting the calculated energy-volume data to the universal Birch–Murnaghan equation of state[31]

$$P = 3B_0 f_{\rm E}(1+2f_{\rm E})^{5/2}\left[1+\frac{3}{2}(B'-4)f_{\rm E} + \frac{3}{2}(B_0B''+(B'-4)(B'-3)+\frac{35}{9})f_{\rm E}^2\right], \tag{3}$$

where $f_{\rm E} = [(V_0/V)^{2/3}-1]/2$. Some thermodynamic properties such as heat capacity C_v, C_P, volume thermal expansion $\alpha_{\rm V}$, bulk modulus B, and Debye temperature $\theta_{\rm D}$ can be determined by

$$C_v = 3nk_{\rm B}\left[4D(\theta_{\rm D}/T) - \frac{3\theta_{\rm D}/T}{{\rm e}^{\theta_{\rm D}/T}-1}\right],$$

$$C_P = C_v(1+\alpha\gamma T), \tag{4}$$

$$\alpha_{\rm V} = \frac{\gamma C_v}{B_T V}, \quad B = -V\left(\frac{\partial P}{\partial V}\right)_{\rm V}(1+\alpha\gamma T), \tag{5}$$

$$\theta_{\rm D} = \frac{h}{2\pi}(6\pi^2 V^{1/2} n)^{1/3} f(\sigma)\sqrt{\frac{B_{\rm S}}{k_{\rm B}^2 M}}, \tag{6}$$

where V, M, n, $B_{\rm S}$, $f(\sigma)$, γ, and $k_{\rm B}$ are the primitive cell volume, the molar mass, the number of atoms per unit cell, the adiabatic bulk modulus, a scaling function that depends on Poisson ratio σ of the isotropic crystal, the Grüneisen parameter, and the Boltzmann's constant, respectively. $D(\theta_{\rm D}/T)$ represents the Debye integral. Detailed expressions of the QHD method can be found in Ref. [30] and references therein.

3. Results and discussions

As a first step, Si_3N_4 are optimized under pressures or not and the results are listed in Table 1. The calculated equilibrium lattice constants are $a = 0.7781$ nm and $c = 0.5641$ nm for α-Si_3N_4, which agree reasonably well with the theoretical and experimental data. The calculated lattice constants are a little larger than the experimental values for α- and β-Si_3N_4. This is due mainly to the fact that GGA usually overestimates lattice constants. The maximum relative error is only 0.47%, which is within the general accuracy of first-principles methods using GGA (usually 1%∼2%). The obtained lattice parameters are very close to the reported values of β-Si_3N_4. The agreement between the computed lattice parameters and other available results is good, indicating that our calculations are valid and reliable.

Table 1. Structural parameters of α- and β-Si_3N_4 compared with the experimental data and other theoretical studies, 1 Å=0.1 nm.

$\alpha-Si_3N_4$					$\beta-Si_3N_4$				
	P/GPa	a/nm	c/nm	V/Å^3		P/GPa	a/nm	c/nm	V/Å^3
This work	0	0.7781	0.5641	295.77	This work	0	0.7632	0.2915	147.06
Theory[32]	0	0.7754	0.5630	–	Theory[32]	0	0.7593	0.2921	–
Theory[15]	0	0.7761	0.5628	293.59	Theory[15]	0	0.7533	0.2934	144.23
Theory[33]	0	0.7818	0.5591	–	Theory[33]	0	0.7595	0.2902	–
Theory[23]	0	0.7792	0.5614	–	Theory[23]	0	0.7622	0.2910	–
Expt.[34]	0	0.7755	0.5621	–	Expt.[34]	0	0.7607	0.2907	–
Expt.[35]	0	0.7766	0.5615	–	Expt.[36]	0	0.7607	0.2911	–

Since pure single crystals of the Si_3N_4 polymorphs are difficult to obtain, very little experimental data are available on the elastic constants. Therefore, we have calculated the elastic constants by using the above-mentioned PW-PP method. According to the Voigt–Reuss–Hill approximations,[37] the polycrystalline bulk modulus B_H, shear modulus G_H, Young's modulus E, Poisson ratio σ, and compressibility K for β-Si_3N_4 can be obtained by

$$B_H = \frac{B_V + B_R}{2}, \quad G_H = \frac{G_V + G_R}{2}, \tag{7}$$

$$E = \frac{9B_H G_H}{3B_H + G_H}, \quad \sigma = \frac{3B_H - 2G_H}{2(3B_H + G_H)}, \tag{8}$$

$$K = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} + 2C_{33} - 4C_{13}}, \tag{9}$$

where the elastic moduli B_V, B_R, B_H, G_V, G_R, and G_H are the Voigt's bulk modulus, Reuss's bulk modulus, Hill's bulk modulus, Voigt's shear modulus, Reuss's shear modulus, and Hill's shear modulus, respectively.[37] The calculated results are listed in Table 2.

Table 2. The bulk modulus B (GPa), elastic constants C_{ij} (GPa), polycrystalline bulk modulus B_H (GPa), shear modulus G_H (GPa), compressibility K (10^{-3}/GPa), Young's modulus E (GPa), B_H/G_H ratio, and Poisson ratio σ of β-Si_3N_4 under pressure P (GPa) or not.

P	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B	B_H	G_H	B_H/G_H	K	E	σ
0	413.8	183.9	102.7	530.8	96.9	114.9	237.3	237.4	121.5	1.954	4.21	311.4	0.281
5	416.1	201.8	117.2	554.5	100.9	107.1	250.5	250.8	120.3	2.083	3.99	311.3	0.293
10	429.5	220.7	132.2	577.1	100.4	104.3	266.8	267.1	119.3	2.238	3.75	311.6	0.306
15	447.7	237.9	154.4	586.1	98.6	104.2	285.6	285.8	117.9	2.424	3.50	310.9	0.318
20	466.4	258.5	168.2	632.3	95.4	103.9	305.2	305.6	117.6	2.598	3.28	312.6	0.329
25	483.4	279.5	184.4	652.9	94.6	101.9	323.1	323.6	116.7	2.773	3.09	312.5	0.339
30	495.8	301.5	201.1	674.8	92.7	97.2	340.5	341.1	113.9	2.995	2.94	307.4	0.349

It is well known that the hardness and strength of solids are related to their elastic moduli. Although β-Si_3N_4 transforms into γ-Si_3N_4 at high pressure and high temperature, the β phase is stable at room temperature up to at least 30 GPa.[2] From Table 1 and Table 2, one can see that a decrease in the lattice constants leads to an enhancement in the bulk modulus. All the elastic constants C_{ij} (except C_{44}) and elastic moduli (except G_H, K, and E) increase monotonously when the pressure is enhanced, but the slopes of their increase differ. K and G_H decrease with applied pressure while C_{44} first increases, and then gradually decreases with increasing pressure. β-Si_3N_4 is almost incompressible at high pressures. According to the Pugh's criterion,[38] a material is ductile if the B/G ratio is larger than 1.75. Our calculations have given the B/G ratios of 1.954∼2.995 at different pressures, suggesting a ductile behavior in β-Si_3N_4.[39] The ductility of β-Si_3N_4 increases with increasing pressure. On the other hand, it is generally believed that the values of the Poisson ratio smaller than 0.1 are associated with covalent compounds, whereas ionic materials have typical values close to 0.25.[40] For ionic solids, the typical relation between bulk and shear modulus is $G/B \approx 0.6$.[41] The G/B ratio and Poisson ratio vary from 0.512 to 0.334 and 0.281∼0.349 in the pressure range of 0 GPa∼30 GPa, respectively. These results imply that the chemical bonding in β-Si_3N_4 is more ionic than covalent, which is in agreement with the results given in Ref. [42]. Born's stability criteria,[43] which reflect the structural stability of materials, are very important here. For the hexagonal lattice, the stability criteria are described as[43]

$$C_{11} > |C_{12}|, \tag{10}$$

$$(C_{11} + C_{12})C_{33} - 2C_{13}^2 > 0, \tag{11}$$

$$C_{44} > 0, \quad C_{66} > 0. \tag{12}$$

The elastic constants listed in Table 2 satisfy all these equations. Therefore, β-Si_3N_4 can retain its mechanical stability in the pressure range of 0 GPa–30 GPa. We do not plot the elastic constants of β-Si_3N_4 at pressures higher than 30 GPa

because β-Si_3N_4 is unstable when $P > 30$ GPa.[2,44]

The experimental data ($C_{11} = 343$ GPa–433 GPa, $C_{12} = 136$ GPa–195 GPa, $C_{13} = 120$ GPa–127 GPa, $C_{33} = 574$ GPa–600 GPa, $C_{44} = 108$ GPa–124 GPa, $C_{66} \cong 119$ GPa)[45,46] and the theoretical values ($C_{11} = 409.3$ GPa, $C_{12} = 271.2$ GPa, $C_{13} = 200.6$ GPa, $C_{33} = 603.6$ GPa, $C_{44} = 108.0$ GPa, $C_{66} = 69.0$ GPa),[15] ($C_{11} = 447.5$ GPa, $C_{12} = 214.6$ GPa, $C_{13} = 165.1$ GPa, $C_{33} = 580.2$ GPa, $C_{44} = 115.0$ GPa, $C_{66} = 116.5$ GPa)[14] are used to compare with our results. Using molecular dynamics, Hirosaki *et al.*[33] have calculated the elastic constants of β-Si_3N_4. Their values are $C_{11} = 591$ GPa, $C_{12} = 182$ GPa, $C_{13} = 162$ GPa, $C_{33} = 690$ GPa, $C_{44} = 189$ GPa, and $C_{66} = 205$ GPa. The experimentally determined elastic constants are widely scattered, because such measurements would require the availability of a single crystal sample of reasonable size. Generally speaking, our calculated elastic constants are in agreement with these results. Considering the fact that GGA usually underestimates bulk modulus, the experimentally measured elastic moduli ($B = 238$ GPa, $E = 306$ GPa, $\sigma = 0.285$,[44] $B = 259$ GPa,[46] $B = 233$ GPa, $G = 123$ GPa,[5,47] and $B = 249$ GPa[48]) and the theoretical values ($B = 262.1$ GPa,[32] $B = 234$ GPa,[49] $B = 232.7$ GPa$\sim$266 GPa[2]) also prove the validity of our calculations.

For a cubic lattice like spinel γ-Si_3N_4, only three independent elastic constants, C_{11}, C_{12}, and C_{44}, are necessary to describe the elastic behavior of the material. The bulk modulus B, Young's modulus E, shear modulus G, Poisson ratio σ, and anisotropy factor A can be derived from[50]

$$E = \frac{9BG}{3B+G}, \quad A = \frac{2C_{44}+C_{12}}{C_{11}},$$
$$\sigma = \frac{E-2G}{2G}, \quad B = \frac{1}{3}(C_{11}+2C_{12}), \tag{13}$$
$$G = \frac{1}{2}\left[\frac{1}{5}(C_{11}-C_{12}+3C_{44}) + \frac{5C_{44}(C_{11}-C_{12})}{4C_{44}+3(C_{11}-C_{12})}\right]. \tag{14}$$

The Kleinman parameter ξ, describes the relative positions of the cation and anion under volume-conserving distortions for which positions are not fixed by symmetry. A low value of ξ implies that there is a large resistance against bond bending or bond-angle distortion and *vice versa*.[51] The Kleinman parameter ξ of γ-Si_3N_4 can be described as[52]

$$\xi = \frac{C_{11}+8C_{12}}{7C_{11}+2C_{12}}. \tag{15}$$

As shown in Table 3, the calculated results are in close agreement with those obtained experimentally and are better than the results obtained by other calculations. The elastic anisotropy of γ-Si_3N_4 is large and the ξ value is relatively high. The calculated B/G ratios, Poisson ratios, and C_{44}/C_{12} ratios are 1.148$\sim$1.544, 0.162$\sim$0.233, and 1.86$\sim$1.19 at different pressures, respectively. The B/G ratio and Poisson ratio suggest a brittle behavior and a covalent bonding nature in γ-Si_3N_4. The chemical bonding strength increases with increasing pressure. The C_{44}/C_{12} ratio indicates the bonding in γ-Si_3N_4 is much more covalent.[11] The elastic moduli B, G, E, and Poisson ratio σ increase with applied pressure increasing. On the other hand, the lattice constant a, the compressibility K, and the anisotropy factor A decrease with applied pressure, which implies that the elastic anisotropy of γ-Si_3N_4 will gradually weaken with the increasing pressure. The elastic anisotropy of γ-Si_3N_4 is large and only weakly pressure dependent. For the cubic lattice, Born's stability criteria under isotropic pressure are judged from the following equation[57]

$$\tilde{C}_{44} > 0, \quad \tilde{C}_{11} > \left|\tilde{C}_{12}\right|, \quad \tilde{C}_{11}+2\tilde{C}_{12} > 0, \tag{16}$$

where $\tilde{C}_{ii} = C_{ii} - P$ $(i = 1,4)$, $\tilde{C}_{12} = C_{12} + P$. The elastic constants of γ-Si_3N_4 satisfy Eq. (16) in the whole pressure interval 0 GPa–50 GPa, which indicates that the cubic γ-Si_3N_4 crystal is stable.

Table 3. Summary of calculated crystal parameters of γ-Si_3N_4 under pressure P (GPa), together with the experimental data and the theoretical results [lattice constant a (Å), elastic constants C_{11}, C_{12}, C_{44} (GPa), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), compressibility K (10^{-3} GPa^{-1}), Poisson ratio σ, Kleinman parameter ξ, and anisotropy factor A].

	P	a	C_{11}	C_{12}	C_{44}	B	G	K	E	A	σ	ξ
This work	0	0.7773	512.1	177.3	330.9	288.9	251.7	3.46	585.2	1.94	0.162	0.490
This work	10 GPa	0.7697	564.0	206.6	347.7	325.8	266.2	3.07	627.6	1.85	0.179	0.508
This work	20 GPa	0.7623	615.4	238.8	363.6	364.4	279.2	2.74	667.2	1.77	0.195	0.528
This work	30 GPa	0.7557	662.3	271.8	377.6	401.9	289.7	2.49	700.9	1.71	0.209	0.548
This work	40 GPa	0.7497	705.8	304.5	390.0	438.2	298.7	2.28	730.2	1.65	0.222	0.566
This work	50 GPa	0.7443	747.6	336.4	400.9	473.4	306.6	2.11	756.7	1.61	0.233	0.582
LDA[11]	0	–	532.6	191.2	341.0	305.0	258.3	–	604.3	1.92	0.169	0.502
LDA[53]	0	0.7664	550.6	191.0	349.4	310.9	264.6	–	618.3	1.90	0.168	0.491
GGA [53]	0	0.7756	499.6	159.0	333.6	272.5	252.0	–	577.8	2.01	0.146	0.464
Calc[9]	$a = 0.7760$	$B = 300$	Calc[1]	$a = 0.7846$	$B = 335$	LDA[54]	$a = 0.7699$	$B = 308$	$G = 258$	$G = 261$[56]		
Force field[32]	$a = 0.5425$	$B = 412$	LDA[3]	$a = 0.7695$	$B = 320$	Expt.[5]	$a = 0.7699$	$B = 290$	$G = 148$	$E = 379$	$\sigma = 0.28$	
LDA[19]	$a = 0.7696$	$B = 321$	GGA[19]	$a = 0.7789$	$B = 285$	Expt.[55]	$a = 0.7728$	$B = 290$–308	$G = 205$–260			

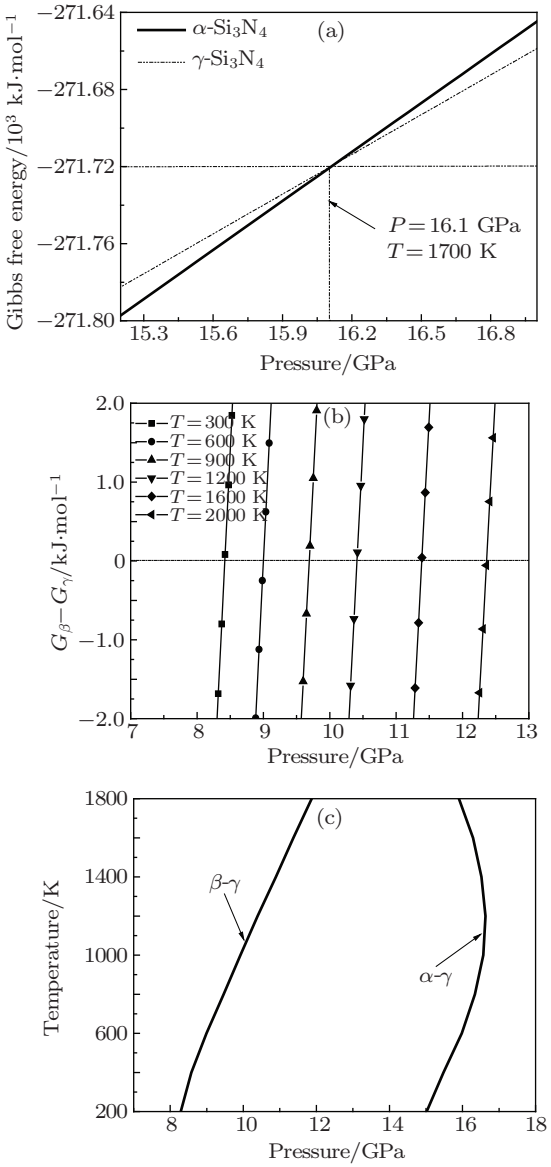


Fig. 1. (a) Plots of Gibbs free energy G versus pressure P for α- and γ-Si_3N_4; (b) The differences of the Gibbs free energies of β- and γ-Si_3N_4 as functions of pressure; (c) T–P phase diagram of α-, β-, and γ-Si_3N_4.

The β phase is the low-temperature phase of the Si_3N_4 polymorphs while γ-Si_3N_4 is the high-temperature phase. Besides, γ-Si_3N_4 can retain its stability under ambient conditions.[9] In order to obtain a deep insight into the phase stability of Si_3N_4, we have carried out calculations of the Gibbs free energy G for the α, β, and γ phases. The Gibbs free energy G as a function of pressure P for each of the α- and γ-Si_3N_4 polymorphs is illustrated in Fig. 1(a). The pressure P, at which the values of Gibbs free energy of both phases are the same, is the critical point for the phase transition. Our calculations imply that α-Si_3N_4 will undergo a structural phase transition to γ-Si_3N_4 at high pressure and temperature. At 1700 K, the thermodynamic requirement for the equality of free energies, suggests that the phase transition from α-Si_3N_4 to γ-Si_3N_4 occurs at 16.1 GPa (see the intersection of the two curves). α-Si_3N_4 has the lower free energy at low pressure while γ-Si_3N_4 has the lower free energy when $P > 16.1$ GPa. This result is in good consistence with the experimental value (17±0.5 GPa at 1673 K∼1873 K) from micro-indentation measurement.[58] Using the VASP code, Xu *et al.*[2] have calculated the phase boundary between α- and γ-Si_3N_4. The transition pressure is found to be 8.3 GPa at 1700 K.[2] Thus, our calculation is close to the experimental data compared with Xu's result.

The pressure dependencies of the Gibbs free energy difference $\Delta G = G_\beta - G_\gamma$ of Si_3N_4 are displayed in Fig. 1(b). At 300 K, ΔG is already negative at low pressure and, consequently, the γ phase appears in the phase diagram. The $\beta \rightarrow \gamma$ phase transition occurs at 8.48 GPa and 300 K, which is in excellent agreement with what had generally been believed.[3,59,60] ΔG increases with applied pressure and eventually becomes positive, indicating the stabilization of γ-Si_3N_4. As shown in Fig. 1(b), the transition pressure increases with increasing temperature.

In Fig. 1(c), we show the calculated phase boundary of Si_3N_4 including the α, β, and γ phases. It is noted that at 300 K, 600 K, 1000 K, 1400 K, and 1800 K, the computed transition pressures for the $\beta \rightarrow \gamma$ phase transition are 8.48, 8.99, 9.92, 10.89, and 11.87 GPa, respectively. At 300 K, our calculated transition pressure agrees well with the data obtained by Zhang *et al.* (10 GPa),[60] Togo *et al.* (13 GPa)[59], Sekine *et al.* (36 GPa),[61] and Kuwabara *et al.* (6.3 GPa).[3] For the $\beta \rightarrow \gamma$ phase transition, the experimentally determined transition pressure P_t varies from 10 GPa to 36 GPa,[2] which is due mainly to different samples (including different impurities and compositions) and different synthesis conditions.[3] The theoretically obtained transition pressures between β- and γ-Si_3N_4 are 10 GPa∼13 GPa (at T = 0∼3000 K),[59] 7.5 GPa∼9 GPa (at T = 300 K∼2000 K),[2] and 5.2 GPa∼6.5 GPa (at T = 300 K∼2400 K).[3] Kuwabara *et al.* have acknowledged the fact that the $\beta \rightarrow \gamma$ transition may be underestimated in Ref. [3]. Our results are in agreement with these investigations. Accordingly, while α- and β-Si_3N_4 are stable at low pressure and γ-Si_3N_4 at high pressure, the Clapeyron slope of the phase boundary between β and γ phases is found to be positive, which indicates γ-Si_3N_4 has lower vibrational entropy at high pressure and temperature. Consequently, higher temperature will require higher pressure for including the phase transformation. For the $\alpha \rightarrow \gamma$ phase transition, the transition pressure changes by less than 2 GPa when the temperature varies from 200 K to 1800 K. It has to be noted, however, that the slope of the phase boundary is quite steep. P_t increases with increasing pressure initially, and then decreases more slowly at high temperature. P_t is not sensitive to the temperature, which suggests that the phase transition is mainly driven by volume variation. According to the

Clausius–Clapeyron relationship,[3] the slope of the phase diagram (dT/dP) is given by $\Delta S/\Delta V$, where ΔS and ΔV are changes in entropy and volume, respectively. Positive slopes indicate that $\beta \to \gamma$ and $\alpha \to \gamma$ transitions are accompanied by the shrinkage of the cell volume. The phase boundaries can be described as

$$P = 8.00944 + 1.13 \times 10^{-3}T + 1.03283 \times 10^{-6}T^2 - 2.60943 \times 10^{-10}T^3, \quad (\beta \to \gamma), \tag{17}$$

$$P = 14.37198 + 3.27 \times 10^{-3}T - 7.83911 \times 10^{-7}T^2 - 3.13552 \times 10^{-10}T^3, \quad (\alpha \to \gamma). \tag{18}$$

Our computed transition pressures for the $\alpha \to \gamma$ phase transformation are 15.22, 15.98, 16.57, 16.52, and 15.90 GPa at temperatures of 300 K, 600 K, 1000 K, 1400 K, and 1800 K, respectively. The $\alpha \to \gamma$ phase boundary obtained by Xu *et al.*[2] is 7 GPa∼8.5 GPa at 300 K∼2300 K. Jiang *et al.*[58] have determined the transition pressure between α- and γ-Si_3N_4 through the micro-indentation measurement (17±0.5 GPa at 1673 K∼1873 K). Nevertheless, the reason for the discrepancy between the present work and Ref. [2] appears to still be unclear. More studies may be required to evaluate the phase boundary between α- and γ-Si_3N_4.

We present the temperature- and pressure-dependent bulk modulus, the inverse of compressibility, for α-, β-, and γ-Si_3N_4 in Fig. 2. The temperature dependencies of the bulk moduli are shown in Fig. 2(a). The bulk modulus B of γ-Si_3N_4 is nearly constant in $T < 200$ K range. When $T > 200$ K, B decreases dramatically as the temperature increases. The cell volume of γ-Si_3N_4 increases and therefore the bulk modulus decreases with increasing temperature. On the other hand, the decreasing trend of the B–T curve (α-Si_3N_4) is very moderate. The bulk modulus of β-Si_3N_4 nearly remains constant when the temperature changes. Concerning α-Si_3N_4, it has a slightly higher bulk modulus than β-Si_3N_4 but much lower bulk modulus than γ-Si_3N_4. The bulk modulus of γ-Si_3N_4 is the largest; α-Si_3N_4 is next, then β-Si_3N_4.

Figures 2(b) and 2(c) show the computed bulk modulus variations with pressure at different temperatures. As expected, B increases monotonically with applied pressure. The relationships between B and P are all linear at various temperatures. For α-, β-, and γ-Si_3N_4, the bulk moduli decrease with increasing temperature at given pressures and increase with applied pressure at certain temperatures. These results are in agreement with the well-known fact that the effect of increasing temperature on a material is the same as decreasing pressure on the same material. Nevertheless, the effect of the temperature on B is less important than that of the pressure. In Fig. 2(b), our results show abrupt changes in bulk modulus around 16.5 GPa, which is believed to be due to a phase transition. At 300 K, the bulk modulus [see Fig. 2(c)] increases gradually up to 8 GPa at which point a dramatic increase of B is seen, which is also believed to be a first-order phase transition between β- and γ-Si_3N_4. The calculated bulk moduli for α-Si_3N_4 are 270 GPa∼287 GPa,[62] 256 GPa,[34] and 242.5 GPa[32] while the experimental values are 228 GPa,[17] 248 GPa,[63] and 282 GPa.[64] These values are in agreement with our calculated values ($B = 234.7$ GPa at 0 K and $B = 233.9$ GPa at 300 K) and the results given in Ref. [3]. On the other hand, good agreement is observed between first-principles bulk modulus and QHD bulk modulus for β- and γ-Si_3N_4.

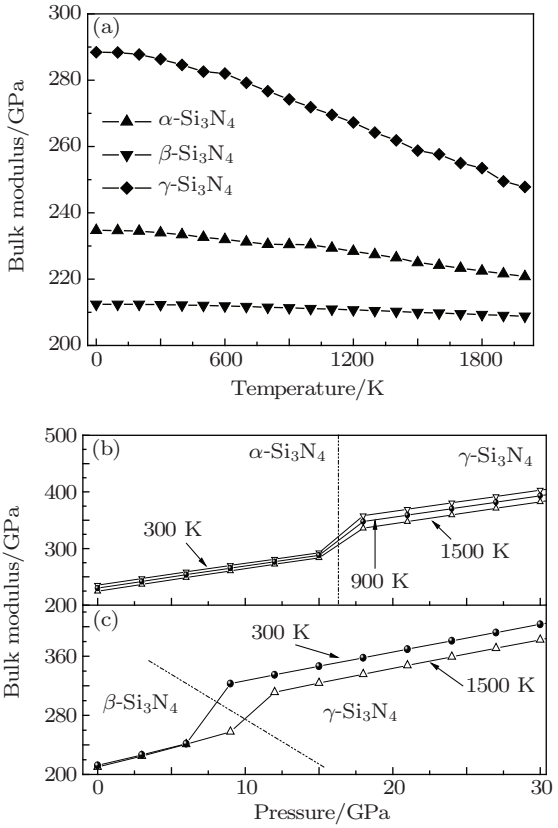


Fig. 2. (a) Bulk moduli of α-, β-, and γ-Si_3N_4 as functions of temperature; panel (b) Pressure dependencies of the bulk moduli for α- and γ-Si_3N_4; (c) The same as panel (b), but for β- and γ-Si_3N_4.

The temperature and pressure dependencies of the volume thermal expansion coefficient α_V of α-, β-, and γ-Si_3N_4 are indicated in Fig. 3. In Fig. 3(a), several interesting features are revealed. Obviously, as temperature increases, α_V increases rapidly and exponentially in the temperature interval 0 K–800 K. Then, α_V gradually begins an almost linear increase at high temperature and the increasing trend is very moderate. The temperature dependence of α_V is very small at high temperature. At a given temperature, α_V decreases with increasing pressure. As pressure increases, the increase of α_V with temperature becomes smaller. At 0 GPa, our calculated α_V (α-Si_3N_4) at 300, 500, 700, 900, 1100, 1500,

and 1800 K are 0.385, 0.591, 0.678, 0.713, 0.744, 0.783, and 0.803×10^{-5}/K, respectively. The calculated α_V at 300, 500, 700, 900, 1100, 1500, and 1800 K are 0.359, 0.716, 0.911, 0.997, 1.045, 1.163, and 1.217×10^{-5}/K,[2] respectively.

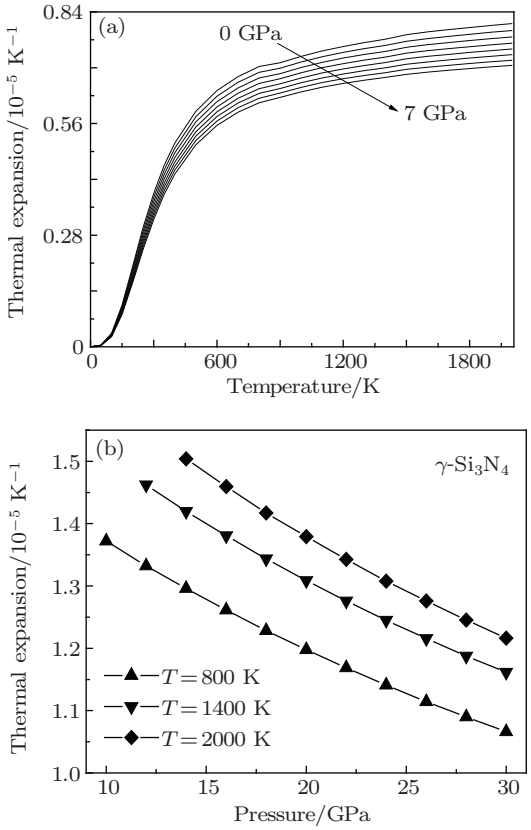


Fig. 3. (a) Thermal expansion coefficient α_V of Si_3N_4 as a function of temperature from 0 up to 7 GPa with 1-GPa interval; (b) Pressure dependence of α_V for γ-Si_3N_4.

We do not plot the thermal expansion coefficient of β-Si_3N_4 because the temperature and pressure dependencies of α_V have been systemically investigated in Refs. [2] and [3]. In Fig. 3(b), it is clearly seen that α_V is sensitive to pressure and temperature. As pressure increases, α_V smoothly decreases and the effect of temperature becomes more important, and a linear behavior appears. Our calculated α_V for γ-Si_3N_4 are 1.091×10^{-5}/K and 1.689×10^{-5}/K at 300 K and 1000 K, respectively. Other calculated values are (1.097×10^{-5}/K at 300 K, 1.949×10^{-5}/K at 1000 K),[2] (1.17×10^{-5}/K at 300 K) [59] and (0.959×10^{-5}/K at 300 K, 1.725×10^{-5}/K at 1000 K).[66] The experimental results are (1.167×10^{-5}/K at 300 K)[65] and (0.815×10^{-5}/K at 300 K, 2.343×10^{-5}/K at 1000 K).[4] The agreement between our values and the other results are excellent. It is interesting to notice that the thermal expansion (α-Si_3N_4) obtained by Xu *et al.* [2] is negative at low temperature. References [66] and [67] and our calculations have found that the thermal expansion (α-Si_3N_4) is positive at low temperature. This is due mainly to the anharmonic approximations of the QHD method, which reflects the limitation of this approach. At sufficiently high temperatures, the anharmonic effects are suppressed and our calculated thermal expansion is in agreement with Xu's results at 0 GPa.[2]

Knowledge of the heat capacity of a solid not only provides essential insight into its vibrational properties but is also mandatory for many applications. The temperature and pressure dependencies of the constant pressure heat capacity C_P for α-, β-, and γ-Si_3N_4 are calculated and displayed in Fig. 4. The evolutions of α-, β-, and γ-Si_3N_4 are similar, i.e.: C_P is very small at low temperature, and approaches a high value at high temperature. The obtained temperature dependencies of heat capacities follow the Debye T^3 law at low temperatures ($T < 800$ K) and gradually approach nearly linear increases at high temperatures ($T > 800$ K), and then the increasing trends become gentler. This is due mainly to the fact that at high temperature the anharmonic effects are suppressed and C_P are very close to constant values. We can see the decreasing trend of C_P while going from γ-Si_3N_4 (highest), α-Si_3N_4 (intermediate), and β-Si_3N_4 (lowest) in Fig. 4(a). The main aspect from these results is the close resemblance in heat capacities of these polymorphs.

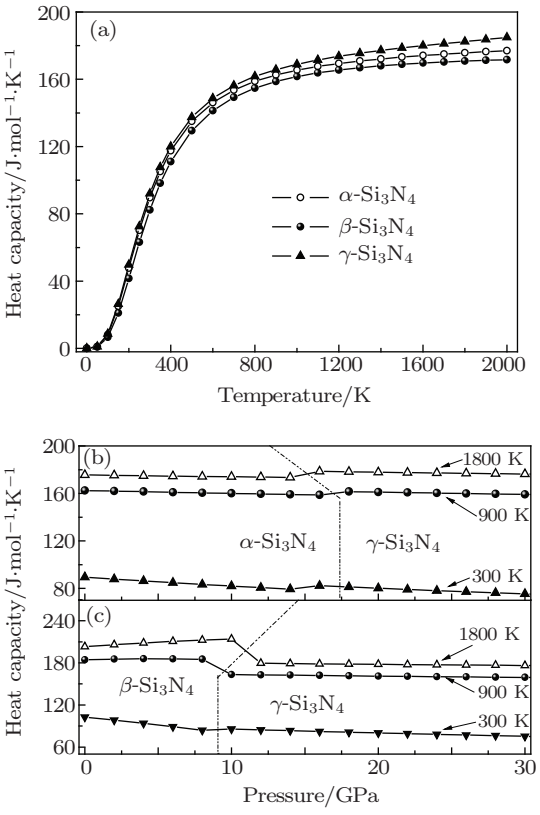


Fig. 4. (a) Temperature dependencies of heat capacity of α-, β-, and γ-Si_3N_4 at 0 GPa; (b) Pressure dependencies of heat capacity in α- and γ-Si_3N_4 considering the phase transition; (c) The same as (b), but for β- and γ-Si_3N_4.

Figures 4(b) and 4(c) show that the heat capacity increases with increasing temperature at a constant pressure, and decreases with applied pressure at a given temperature. The effect of the temperature on C_P is more significant than that of the pressure. In Fig. 4(b), C_P decreases linearly with applied

pressure. There are discontinuity points ($P = 14$ GPa$\sim$18 GPa for different temperatures) in the C_P–P curves, which are similar to that of bulk modulus. In Fig. 4(c), the discontinuity points appear at 8 GPa$\sim$12 GPa for different temperatures, which are believed to indicate first-order phase transitions. We do not plot the heat capacities of β-Si_3N_4 at pressures higher than 10 GPa because the β phase starts to show signs of structural instability.[2,12] The calculated heat capacity of γ-Si_3N_4 are 92.79 J/mol·K and 166.95 J/mol·K at 300 K and 1000 K,[55] respectively. The calculated C_P for β-Si_3N_4 is 111.54 J/mol·K.[48] Our calculated C_P are 92.26 J/mol·K (300 K, γ-Si_3N_4), 169.18 J/mol·K (1000 K, γ-Si_3N_4), and 111.02 J/mol·K (400 K, β-Si_3N_4). Our results are in excellent agreement with both the experimental data and theoretical results. There are no experimental data or theoretical results for β- and γ-Si_3N_4 at high pressure. To the authors' knowledge, no other data about α-Si_3N_4 are available for us to compare with.

It is worth noting that the contributions of the thermal electrons at finite temperature are not taken into account in the quasi-harmonic Debye model — only vibrations are considered. Therefore, the QHD model is not suitable for some transition metals and very narrow gap semiconductors. Usually, the quasi-harmonic Debye model is not valid when the temperature is relatively near to the melting point of the material. For the Si_3N_4 polymorphs, we think that the QHD method may not be valid at temperatures higher than 1800 K. On the other hand, the measurements of the thermodynamic properties of Si_3N_4 are taken from samples including porosities and defects. In this paper, however, all calculations we have presented are related to ideal crystal. Therefore, our calculated fundamental properties of the Si_3N_4 polymorphs should be validated by experiments in the near future.

4. Conclusions

The equilibrium structure, elastic moduli, thermodynamic properties, and phase transition characters of the binary α-, β-, and γ-Si_3N_4 compounds have been extensively investigated by using the plane-wave pseudo-potential method in combination with the QHD method. It is also seen that the QHD method generates acceptable results at high temperatures. The most relevant results can be summarized as follows:

i) β- and γ-Si_3N_4 are mechanically stable at 0 GPa–30 GPa and 0 GPa–50 GPa, respectively. β-Si_3N_4 is a hard material with less compressibility compared to other nitrides, which also exhibits ductile behavior and ionic chemical bonding. γ-Si_3N_4 is also found to be a hard material with a high bulk modulus, covalent bonding, and brittle behavior, especially at high pressure.

ii) Applied temperature leads to a nearly linear increase of the phase boundary between β- and γ-Si_3N_4. The phase boundaries can be described as $P = 8.00944 + 1.13 \times 10^{-3}T + 1.03283 \times 10^{-6}T^2$–$2.60943 \times 10^{-10}T^3$, $(\beta \to \gamma)$ and $P = 14.37198 + 3.27 \times 10^{-3}T$–$7.83911 \times 10^{-7}T^2 - 3.13552 \times 10^{-10}T^3$, $(\alpha \to \gamma)$. Positive slopes indicate that $\beta \to \gamma$ and $\alpha \to \gamma$ transitions are accompanied by the shrinkage of cell volume. More importantly, the phase transitions are not sensitive to temperature.

iii) Thermal and pressure effects on some macroscopic properties of Si_3N_4 are predicted in the ranges of 0 K–2000 K and 0 GPa–30 GPa. α-, β-, and γ-Si_3N_4 have very close evolutions of their heat capacities C_P with temperature. C_P increases sharply with increasing temperature first, and then the propensity of increment becomes moderate. The thermal expansion α_V is shown to converge to a constant value at high temperature. While γ-Si_3N_4 has a larger bulk modulus than α-Si_3N_4, its α_V is also larger. The result shown in this paper is part of more extensive theoretical efforts to explore the properties of ultra-hard, N-based materials, but we still await experimental confirmations.

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