

Investigations of high-pressure and high-temperature behaviors of the newly-discovered willemite-II and post-phenacite silicon nitrides*

Chen Dong(陈 东)[†]

College of Physics and Electronic Engineering, Xinyang Normal University, Xinyang 464000, China

(Received 23 March 2013; revised manuscript received 13 May 2013)

Using the first-principles method of the plane-wave pseudo-potential, the structural properties of the newly-discovered willemite-II Si_3N_4 (wII phase) and post-phenacite Si_3N_4 (δ phase) are investigated. The α phase is predicted to undergo a first-order $\alpha \rightarrow$ wII phase transition at 18.6 GPa and 300 K. Within the quasi-harmonic approximation (QHA), the $\alpha \rightarrow$ wII phase boundary is also obtained. When the well-known $\beta \rightarrow \gamma$ transition is suppressed by some kinetic reasons, the $\beta \rightarrow \delta$ phase transformation could be observed in the phase diagram. Besides, the temperature dependences of the cell volume, thermal expansion coefficient, bulk modulus, specific heat, entropy and Debye temperature of the involved phases are determined from the non-equilibrium free energies. The thermal expansion coefficients of wII- Si_3N_4 show no negative values in a pressure range of 0–30 GPa, which implies that the wII- Si_3N_4 is mechanically stable. More importantly, the δ - Si_3N_4 is found to be a negative thermal expansion material. Further experimental investigations may be required to determine the physical properties of wII- and δ - Si_3N_4 with higher reliability.

Keywords: first-principles, nitrides, phase boundary, thermal property**PACS:** 63.20.dk, 81.05.Je, 81.30.-t, 65.40.-b**DOI:** 10.1088/1674-1056/22/12/126301

1. Introduction

Silicon nitride (Si_3N_4), which belongs to the group IV nitrides, is currently the well-known technological material, owing to its outstanding mechanical and thermal properties.^[1] Due to its hardness, corrosion resistance, oxidation resistance, ability to withstand high temperature and high compressibility, Si_3N_4 plays an important role in the modern development of condensed-matter physics.^[2,3] Si_3N_4 can also be used as dielectrics, reactors, engines, and green/blue-UV LEDs.^[4–6] The two basic structures, named α and β phases, have been the only two known Si_3N_4 polymorphs for a long time. α - and β - Si_3N_4 have hexagonal structures and only differ along the Z axis in the stacking sequence. It is generally believed that the β configuration is the low-temperature phase of Si_3N_4 and the α one is the meta-stable phase of Si_3N_4 .^[7,8] A third form of Si_3N_4 with a spinel lattice (γ phase) has been synthesized by the diamond anvil cell technique,^[9] which has a hardness comparable to the hardest oxide (stishovite).^[10] The willemite-II structure was first reported as a low-compressible modification of C_3N_4 . Recently, the willemite-II Si_3N_4 (wII phase) was discovered by scientists.^[11] β - Si_3N_4 can exist at pressures up to 34 GPa and then transforms to an unknown phase (δ - Si_3N_4) under further compression.^[7,12]

Togo and Kroll^[13] have investigated the phase boundary between β - and γ - Si_3N_4 using lattice dynamics. The calculated transition pressure P_t is about 11 GPa~13 GPa between 0 and 3000 K. Kuwabara *et al.*^[8] found that the

transition pressure of the $\beta \rightarrow \gamma$ transition is 5 GPa~7 GPa (0~2300 K) through first-principles calculations. More importantly, Xu *et al.*^[7] found that δ - Si_3N_4 crystallizes into the “post-phenacite” structure and the $\beta \rightarrow \delta$ transition would occur at 35 GPa~36 GPa and 300 K. There is a great deal of research work on the crystal structures and thermal properties of α - Si_3N_4 (lattice parameter,^[3,10] specific heat,^[8,10,14] thermal expansion,^[7,8,10] entropy,^[14] bulk modulus,^[3,8,10,15] β - Si_3N_4 (lattice parameter,^[10,13] specific heat,^[8,10,14] thermal expansion,^[7,8,10] entropy,^[14] bulk modulus,^[8,10,13,15] Grüneisen parameter^[7]) and γ - Si_3N_4 (lattice parameter,^[10,13,16,17] specific heat,^[8,10,18] thermal expansion,^[7,8,10,17,18] entropy,^[18] bulk modulus^[8,10,13,18,19]). Besides, the electronic properties of these polymorphs are discussed in Refs. [20]–[22]. Nevertheless, wII- and δ - Si_3N_4 are far less studied than their counterparts α -, β -, and γ - Si_3N_4 .

Although the phase stability of Si_3N_4 has been investigated by different scientists,^[7,8,13] only few of them considered the $\beta \rightarrow \delta$ phase transition. The reasons may be as follows. (i) It is difficult to synthesize δ - Si_3N_4 because extremely high pressures are needed. (ii) Only when the equilibrium $\beta \rightarrow \gamma$ phase transition ($P_t = 7 \sim 9$ GPa^[7] or 11 GPa~13 GPa^[13]) is bypassed due to kinetic reasons, the $\beta \rightarrow \delta$ transition could be observed in the phase diagram. Recently, the $\beta \rightarrow$ wII phase transition has been discovered by Kroll.^[11] Due to the identical bonding and very similar long range lattice structures between α and β phases, the $\alpha \rightarrow$ wII phase transition is likely to occur at certain pressures and tem-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11005088 and 11105115), the Key Project of Henan Educational Committee, China (Grant No. 12A140010), and the Special Foundation for Young Teacher of Xinyang Normal University, China (Grant No. 2011084).

[†]Corresponding author. E-mail: chchendong2010@163.com

peratures. In this paper, we address the temperature–pressure phase diagrams of the newly-discovered polymorphs and, explicitly, calculate the thermal properties as functions of temperature.

2. Benchmark calculations

We adopt the plane-wave pseudo-potential method together with ultrasoft pseudo-potential (US-PP),^[23] which is implemented in the Quantum ESPRESSO package.^[24] The generalized gradient approximation GGA-PBE is chosen for the exchange–correlation functional.^[25] Our calculation includes full relaxation of atomic positions and optimization of cell geometries. Reference configurations for the valence electrons are Si-3s²3p² and N-2s²2p³. Convergence tests guided the choice of 500 eV (α -Si₃N₄), 480 eV (wII-Si₃N₄), 500 eV (β -Si₃N₄), and 450 eV (δ -Si₃N₄) for the cutoff energies. The k -point meshes, based on the Monkhorst–Pack scheme,^[26] are 4×4×7 (α -Si₃N₄), 4×4×12 (β -Si₃N₄), 10×10×10 (wII-Si₃N₄) and 6×6×15 (δ -Si₃N₄). The total energies are converged to at least 10⁻⁶ eV/atom.

According to the quasi-harmonic approximation (QHA), the non-equilibrium Gibbs free energy $G^*(V; P, T)$ can be written as^[27]

$$G^*(V; P, T) = E(V) + PV + A_{\text{vib}}(T, \theta_{\text{D}}(V)), \quad (1)$$

where $E(V)$ are the total energies at different volumes; V , P , and T are the cell volume, pressure, and temperature, respectively; PV corresponds to the constant hydrostatic pressure; A_{vib} is the vibrational Helmholtz free energy; $\theta_{\text{D}}(V)$ is the Debye temperature at different volumes V . Series standard thermodynamic parameters can be determined by fitting the calculated energy–volume data to the Birch–Murnaghan equation of state (EOS)^[28]

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

where $f_{\text{E}} = [(V_0/V)^{2/3} - 1]/2$; B_0 represents the zero pressure bulk modulus; B' and B'' are the first-order pressure derivative and second-order derivative of B , respectively; C_v and C_p are the specific heat, S is the entropy, $\alpha(T)$ the volume thermal expansion coefficient and θ_{D} the Debye temperature, which can be described, respectively, as

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

$$C_p = C_v (1 + \alpha\gamma T), \quad (4)$$

$$S = nk \left[4D(\theta_{\text{D}}/T) - 3 \ln(1 - e^{-\theta_{\text{D}}/T}) \right], \quad \alpha = \frac{\gamma C_v}{B_T V}, \quad (4)$$

$$\theta_{\text{D}} = \frac{h}{2\pi} (6\pi^2 V^{1/2} n)^{1/3} f(\sigma) \sqrt{\frac{B_{\text{S}}}{M k_{\text{B}}^2}}, \quad (5)$$

where M , n , B_{S} , B_{T} , $f(\sigma)$, γ , h , and k_{B} are the molar mass, the number of atoms per unit cell, the adiabatic bulk modulus, the isothermal bulk modulus, a scaling function that depends on Poisson ratio σ of the isotropic crystal, the Grüneisen parameter, the Planck constant, and the Boltzmann constant, respectively; $D(\theta_{\text{D}}/T)$ represents the Debye integral.^[27] A detailed expression of the QHA scheme can be found in Ref. [27].

3. Results and discussion

3.1. Crystal structures

In Table 1, we show the calculated parameters for wII- and δ -Si₃N₄. Since the lattice constant and elastic constants of wII-Si₃N₄ vary linearly with applied pressure, we only give the results at 0 GPa and 40 GPa. The lattice constant a and internal coordinate u decrease with applied pressure while the elastic constants C_{ij} and bulk modulus B show the opposite trend. a and u are in good agreement with the results given in Ref. [11]. For a cubic lattice, the Born stability criteria^[29] can be written as

$$C_{44} > 0, \quad C_{11} > |C_{12}|, \quad C_{11} + 2C_{12} > 0. \quad (6)$$

Table 1. Computed values of lattice constant a , elastic constant C_{ij} , bulk modulus B , internal coordinate u for wII-Si₃N₄, and the lattice constants a and c and cell volume V for δ -Si₃N₄.

wII-Si ₃ N ₄			δ -Si ₃ N ₄					
P/GPa			P/GPa	u	P/GPa	a/nm	c/nm	$V/\text{\AA}^3$
0	C_{11}/GPa	374.7	0	0.0314	35	0.7024	0.2721	116.29
0	C_{12}/GPa	190.5	5	0.0309	40	0.6985	0.2704	114.25
0	C_{44}/GPa	213.6	10	0.0301	45	0.6948	0.2694	112.63
0	B/GPa	251.9	15	0.0293	50	0.6913	0.2684	111.10
0	a/nm	0.6465	20	0.0284	55	0.6880	0.2675	109.65
40	a/nm	0.6195	25	0.0276	60	0.6849	0.2666	108.28
40	C_{11}/GPa	452.9	30	0.0267	–	–	–	–
40	C_{12}/GPa	329.5	35	0.0256	–	–	–	–
40	C_{44}/GPa	249.0	40	0.0245	–	–	–	–
40	B/GPa	370.7	–	–	–	–	–	–
0	VASP ^[11]	$a = 0.6475 \text{ nm}^{[11]}$	0	0.0314 ^[11]	–	–	–	–

The elastic strain, which is used in our elastic constant calculations, is defined in Euler notation.^[30] Therefore, the simple Born criteria (without pressure) can be used to judge the elastic stability of our system. The elastic constants satisfy Eq. (6), which means that the wII phase can retain its stability in a pressure range of 0–40 GPa. The lattice parameters a and c and the cell volume V of δ -Si₃N₄ decrease with pressure increasing, but the slopes are different. Unfortunately, there are no experimental data or theoretical results available related to the elastic constants of wII-Si₃N₄ and lattice constants of δ -Si₃N₄. Besides, the ground state lattice parameters of α - and β -Si₃N₄ can be found in our previous publications.^[31,32] More importantly, the current knowledge of the hypothesized polymorphs of Si₃N₄ and the relationships between these phases are sketched in Fig. 1.

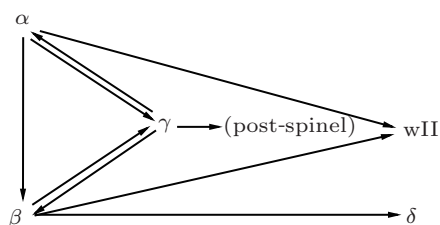


Fig. 1. Currently known polymorphs of Si₃N₄.

As is well known, the phase transition pressure can be developed from the usual condition of equal Gibbs free energies,

i.e., at the critical pressure P_t , the values of Gibbs free energy, G , of the two polymorphs are the same. As shown in Fig. 2(a), Si₃N₄ undergoes a structural phase transition from the α phase to the wII phase. The intercross point of the free energy curves indicates that the $\alpha \rightarrow$ wII transformation occurs at 18.6 GPa and 300 K. α -Si₃N₄ has the lower Gibbs free energy at low pressure ($P < 18.6$ GPa) and the wII phase would be favored at $P > 18.6$ GPa. This is in agreement with the fact that α -Si₃N₄ is the meta-stable phase of Si₃N₄.^[7,8,33]

In Fig. 2(b), we plot the pressure–temperature phase diagram of Si₃N₄ including two polymorphs α - and wII-Si₃N₄. At 0 K, 300 K, 500 K, 700 K, and 900 K, the calculated transition pressures are 19.0, 18.6, 17.5, 15.5 and 12.8 GPa, respectively. The critical pressure of the $\alpha \rightarrow$ wII transition decreases nonlinearly with the increase of temperature. A negative slope has been found. Consequently, higher temperatures will require lower pressures for the $\alpha \rightarrow$ wII phase transformation. P_t changes by more than 7.7 GPa between 0 K and 1000 K, which implies that the $\alpha \rightarrow$ wII transition is sensitive to temperature. Kroll^[11] has determined the $\beta \rightarrow$ wII transition pressure ($P_t = 20$ GPa at 0 K) using first-principles calculations. The critical pressure of $\beta \rightarrow$ wII transition is also given in our previous paper (20.8 GPa at 300 K).^[34] Unfortunately, there are no available experimental data or theoretical results related to the $\alpha \rightarrow$ wII phase boundary for us to compare with. Therefore, our work is the first attempt in this direction.

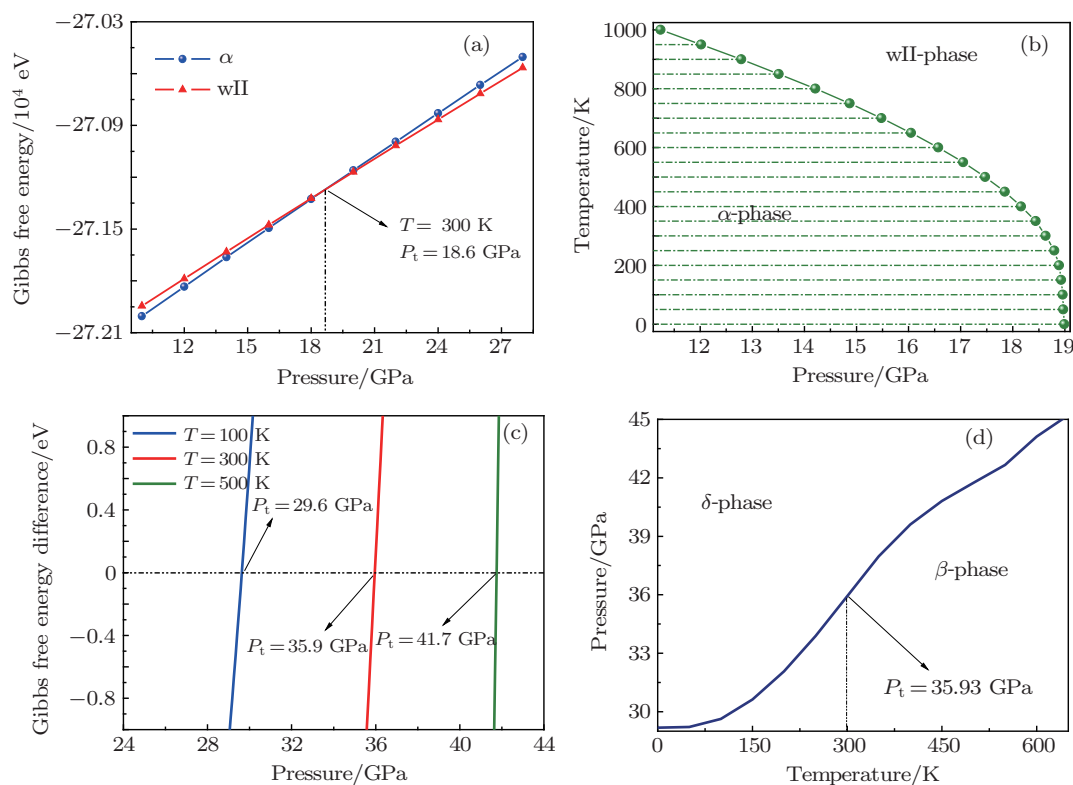


Fig. 2. (color online) Curves of Gibbs free energy versus pressure for α - and wII-Si₃N₄ at 300 K (a) phase boundary between the α and wII phases, (b) Gibbs free energy difference between the β and δ polymorphs (c) and phase boundary between β - and δ -Si₃N₄ (d).

The curves of Gibbs free energy difference ΔG ($\Delta G = G_\beta - G_\delta$) versus pressure for Si_3N_4 in the β and δ phases are shown in Fig. 2(c). At 29.6 GPa and 100 K, the Gibbs free energies are the same, which shows that the phase transformation occurs at this point. ΔG remains negative at pressures up to 29.6 GPa and, consequently, the δ phase appears in the phase diagram. δ - Si_3N_4 stabilizes with smaller Gibbs free energy than β - Si_3N_4 does at high pressures. The values of P_t are 29.6, 35.9, and 41.7 GPa at temperatures of 100 K, 300 K, and 500 K, respectively. At 300 K, the calculated value of P_t accords well with the synchrotron angle-dispersive x-ray diffraction data (35 GPa~36 GPa).^[7]

The computed P - T phase diagram of β - and δ - Si_3N_4 is drawn in Fig. 2(d). The transition pressure increases nonlinearly with the increase of temperature. It should be noted, however, that the slope of the phase boundary is steep. The positive slope indicates that at higher temperatures higher pressures are required for the $\beta \rightarrow \delta$ phase transition. According to the Clausius–Clapeyron relationship,^[8] the $\beta \rightarrow \delta$ phase transition is accompanied by the shrinkage of the lattice. The phase boundaries can be described as

$$P = 18.90352 + 2.17 \times 10^{-3}T - 1.04817 \times 10^{-5}T^2 + 5.98202 \times 10^{-10}T^3, \quad (\alpha \rightarrow \text{wII}), \quad (7)$$

$$P = 28.90824 + 5.9893 \times 10^{-4}T + 1.03715 \times 10^{-4}T^2 - 1.03472 \times 10^{-7}T^3, \quad (\beta \rightarrow \delta). \quad (8)$$

In Fig. 3(a), we illustrate the dependences of cell volume V and normalized volume V/V_0 on the pressure P (V_0 is the zero pressure equilibrium cell volume). The temperature effects on V/V_0 are not as significant as on V . This is in agreement with the fact that the effect of increasing pressure on wII- Si_3N_4 is the same as the case of reducing its temperature. In Fig. 3(b), we present the variations in the volume thermal expansion coefficient $\alpha(T)$ each as a function of temperature for wII- Si_3N_4 . The values of $\alpha(T)$ are very low in a low temperature region ($T < 100$ K). After the sharp increase between 100 K and 600 K, $\alpha(T)$ increases almost linearly with temperature increasing, but slower, above 600 K. At a given temperature, $\alpha(T)$ decreases quickly with applied pressure increasing. Besides, the temperature dependences of the constant-pressure specific heat C_P are plotted in Fig. 3(c). At low temperatures, C_P is proportional to T^3 , which is in agreement with the Debye- T^3 law.^[35] At sufficiently high temperatures, the anharmonic effects are suppressed and C_P increases linearly with the increase of temperature. Unlike the constant volume specific heat (C_V), C_P follows a linear increase at high temperatures while C_V approaches to a constant value (the Dulong–Petit limit).^[36] At a given temperature, C_P decreases with applied pressure increasing.

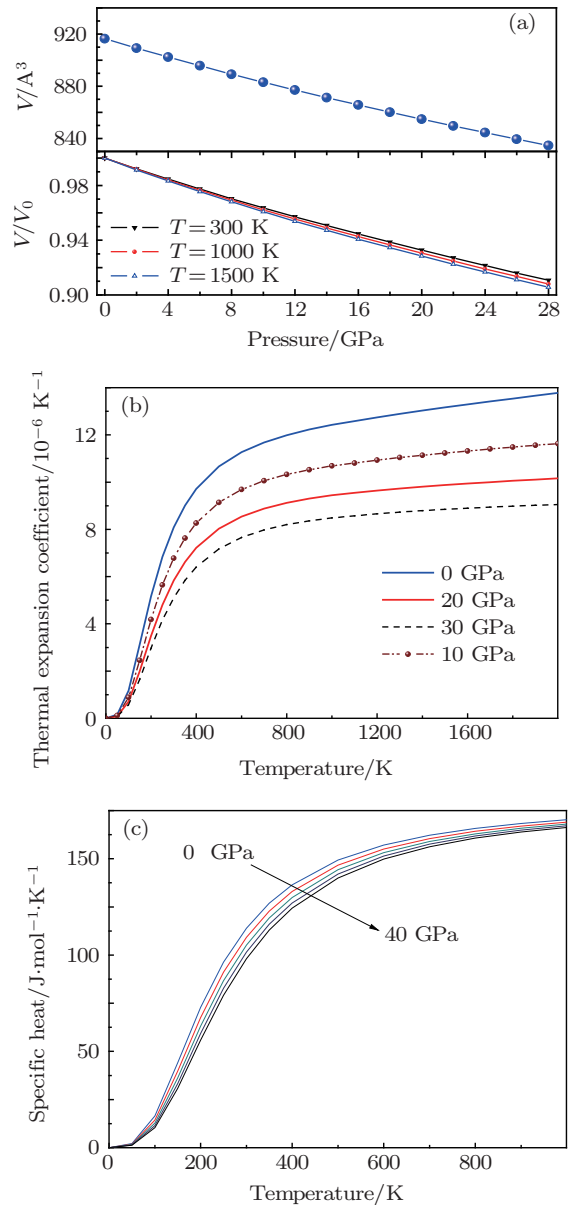


Fig. 3. (color online) Calculated temperature dependences of the cell volume V at 300 K and normalized volume V/V_0 of wII- Si_3N_4 (a) the thermal expansion coefficient α and (b) specific heat C_P (c) at different pressures for wII- Si_3N_4 .

Figures 4(a) and 4(b) show the entropy and specific heat of δ - Si_3N_4 each as a function of temperature up to 1900 K at 40 GPa. S is fairly constant when $T < 200$ K. Between 200 K and 600 K, the entropy, as expected, increases sharply with temperature increasing and the increment becomes moderate in the temperature range of 600 K–1900 K. C_V increases with T^3 at low temperatures. The slope of the C_V - T curve is much greater before a knee point (at 600 K) than after it. At high temperatures, the anharmonic effects on C_V are restrained. C_V increases linearly and gradually approaches to the Dulong–Petit limit 174.6 J/mol·K ($3R$ for monoatomic solids).^[36] The variations of Debye temperature θ_D and bulk modulus B with pressure are shown in Fig. 4(c). θ_D and B decrease by 5.2% and 16.8% in the pressure range of 36 GPa–44 GPa, respectively. The pressure effect on θ_D is not as significant

as on B . The calculated entropy S , bulk modulus B , specific heat C_v , thermal expansion coefficient $\alpha(T)$, and Debye temperature θ_D are 35.1 J/mol·K, 161.3 GPa, 74.2 J/mol·K, $-8.91 \times 10^{-6} \text{ K}^{-1}$, and 1291.8 K at 40 GPa and 300 K, respectively. B and θ_D decrease with pressure increasing, which indicates that δ -Si₃N₄ is a negative thermal expansion material.

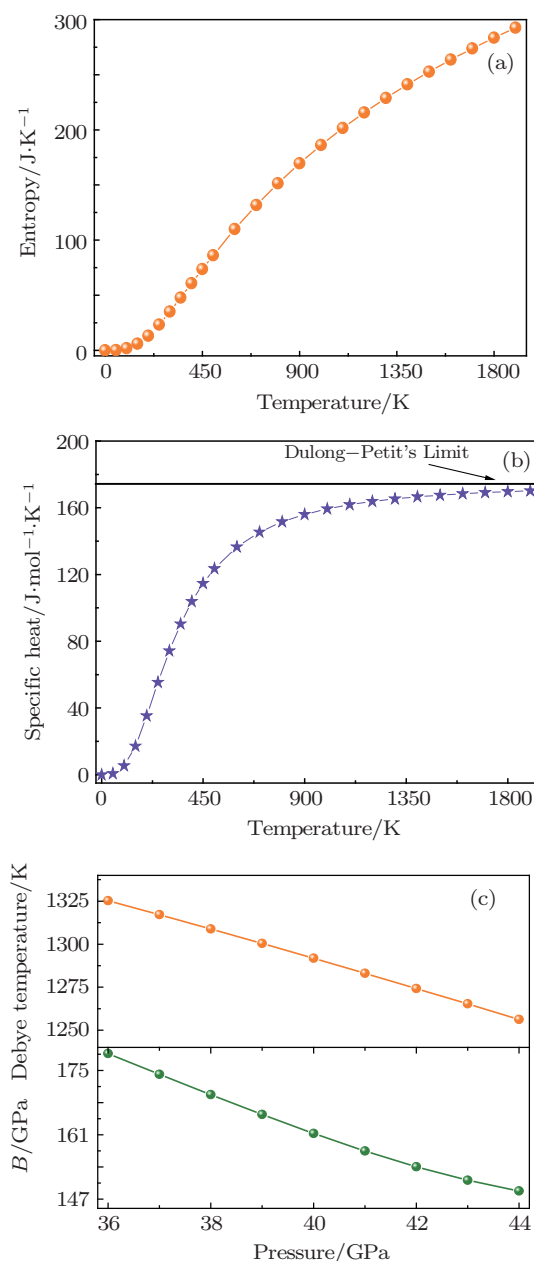


Fig. 4. (color online) Temperature-dependent entropy S (a) and specific heat C_v (b) of δ -Si₃N₄ at 40 GPa; the pressure-dependent Debye temperature θ_D and bulk modulus B of δ -Si₃N₄ at 300 K (c).

4. Conclusions

In this paper, we calculate the ground-state properties including structural parameters, lattice constants, and elastic constants of the newly-discovered wII- and δ -Si₃N₄ polymorphs through the plane-wave pseudo-potential method, together with their thermal properties and phase transition char-

acteristics. The main results can be summarized as follows.

(i) The calculated lattice constant and internal coordinate of wII-Si₃N₄ are in excellent agreement with the calculated results given in Ref. [11] (using VASP code). The elastic constants show that wII-Si₃N₄ can retain its mechanical stability in a pressure range of 0–40 GPa.

(ii) The equilibrium $\alpha \rightarrow$ wII and $\beta \rightarrow \delta$ transformation pressures are found to be 18.6 GPa (at 300 K) and 35.9 GPa (at 300 K), respectively. The $\beta \rightarrow \delta$ phase boundary has a positive gradient, which means that at higher temperatures it needs a higher pressure to synthesize δ -Si₃N₄. The bulk modulus and Debye temperature of δ -Si₃N₄ decrease with the applied pressure increasing, which indicates that δ -Si₃N₄ belongs to negative thermal expansion materials.

(iii) Applying the quasi-harmonic approximation, some thermal properties like specific heat C_v , C_p , entropy S , thermal expansion coefficient $\alpha(T)$, bulk modulus B , and Debye temperature θ_D are successfully determined in a temperature range of 0–1500 K.

Acknowledgment

The author is grateful to Prof. M. A. Blanco and his colleagues for their Gibbs code.

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