Phase Transition Characters and Thermodynamics Modeling of the Newly-Discovered wII- and Post-Spinel Si_3N_4 Polymorphs: A First-Principles Investigation

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The equilibrium lattice constants, elastic constants and elastic moduli of wII- and post-spinel Si_3N_4 have been investigated in the pressure ranges of 0–40 GPa and 160–240 GPa, respectively. These two phases are found to be dynamically stable. The post-spinel phase is one of the strongest materials yet investigated under extreme compressions. Some fundamental properties and phase transition characters are evaluated from the quasi-harmonic approximation. The transition pressures from the γ phase to the post-spinel phase are 152.5 GPa (at 300 K) and 181.8 GPa (at 1500 K). The phase transition pressures of the $\beta \rightarrow \text{wII}$ and $\gamma \rightarrow \text{post-spinel}$ transitions increase with the rise of temperature; hence, at higher temperature it requires higher pressure to synthesize post-spinel Si_3N_4 . The heat capacity, thermal expansion and bulk modulus of the new phases are computed as functions of pressure and temperature. The heat capacity of post-spinel Si_3N_4 is large at high temperature and only weakly pressure dependent.

KEY WORDS: First-principles; Nitride; Elastic constant; Phase transition

1. Introduction

Silicon nitride (Si_3N_4), which belongs to the family of group IV nitrides, is an important technical material as a ceramic and a dielectric insulator^[1]. Si_3N_4 has found practical applications in motors, cutting tools, antifriction bearings and gas engines due to its outstanding mechanical property, good corrosion resistance, high decomposition temperature and good thermal stability^[2]. Besides, its low density, excellent oxidation resistance, tunable electrical conductivity and suitable fracture toughness lead to numerous applications in modern industry and space project^[3].

For a long time, the hexagonal α and β phases are the two known polymorphs for Si_3N_4 . The third polymorph (γ phase) was recently discovered by Zerr *et al.*^[4] γ - Si_3N_4 shows cubic spinel-type structure,

having some sixfold-coordinated Si atoms, which is greatly different from the conventional α and β phase with only fourfold-coordinated Si atoms^[5]. These three phases have been investigated by experiments^[6–8] and theorists^[8–11]. The willemite-II structure was first proposed as a low-compressible phase of C_3N_4 ^[12]. For Si_3N_4 , there also exists a willemite-II phase (wII- Si_3N_4)^[13]. The wII phase was never directly synthesized by experiments because it has no region within the pressure-enthalpy phase diagram. If the $\beta \rightarrow \gamma$ transition can be ignored by some mechanism reasons, we will observe the $\beta \rightarrow \text{wII}$ transformation^[13]. Recently, Si_3N_4 is found to transform to a high pressure phase beyond spinel, namely the “post-spinel” phase. The crystal structures and atomic coordinations of these phases can be found in Refs. [13–15]. Due to the difficulty of synthesis in experiments, the fundamental properties of the wII- and post-spinel phases are lack.

The two main aspects of this study are: (1) What are the phase boundaries of the $\gamma \rightarrow \text{post-spinel}$ and $\beta \rightarrow \text{wII}$ transformations? (2) The fundamental

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structural, elastic, thermodynamic properties and the temperature dependences of these new polymorphs.

2. Benchmark Calculations

We adopt the famous plane-wave pseudo-potential method with ultrasoft pseudo-potentials (US-PP)^[16]. The generalized gradient approximation GGA-PBE is chosen for the exchange-correlation potential^[17]. Our calculation includes full relaxation of atomic coordinates 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 (β -Si₃N₄), 480 eV (wII-Si₃N₄), 500 eV (γ -Si₃N₄) and 460 eV (post-spinel Si₃N₄) for the energy cutoffs. The k-point meshes, based on the Monkhorst-Pack scheme^[18], are 4×4×12 for β -Si₃N₄, 10×10×10 for wII-Si₃N₄, 8×8×8 for γ -Si₃N₄ and 7×7×7 for post-spinel Si₃N₄, respectively. Equilibrium structures of Si₃N₄ are optimized until the total energies are converged to at least 10⁻⁶ eV/atom.

According to the quasi-harmonic Debye approximation, the non-equilibrium Gibbs free energy $G^*(V, P, T)$ can be written as^[19]

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

where PV corresponds to the constant hydrostatic pressure. A_{vib} is the vibrational Helmholtz free energy. Series standard thermodynamics can be determined by fitting the calculated energy-volume data to the universal Birch-Murnaghan equation of state (EOS)^[20]

$$P = 3B_0 f_E (1 + 2f_E)^{\frac{5}{2}} [1 + \frac{3}{2}(B' - 4)f_E + \frac{3}{2}(B_0 B'' + (B' - 4)(B' - 3) + \frac{35}{9})f_E^2] \quad (2)$$

where $f_E = [(V_0/V)^{2/3} - 1]/2$. The heat capacity C_V , C_p , volume thermal expansion α and Debye temperature θ_D can be described as

$$C_V = 3nk_B \left[4D(\theta_D/T) - \frac{3\theta_D/T}{e^{\theta_D/T} - 1} \right],$$

$$C_p = C_V(1 + \alpha\gamma T) \quad (3)$$

$$\alpha = \frac{\gamma C_V}{B_S V}(1 + \alpha\gamma T),$$

$$\theta_D = \frac{h}{2\pi} (6\pi^2 V^{1/2} n)^{1/3} f(\sigma) \sqrt{\frac{B_S}{k_B^2 M}} \quad (4)$$

where V , M , n , B_S , $f(\sigma)$, γ and k_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 , the Grüneisen parameter and the Boltzmann constant, respectively. $D(\theta_D/T)$ represents the Debye integral. Detailed expression of this scheme can be found in Ref. [19].

3. Results and Discussion

3.1 Crystal structures

Table 1 shows the optimized lattice constants, elastic constants and elastic moduli of wII-Si₃N₄ at different pressures, together with the calculated lattice constant listed in Ref. [13]. The lattice constant a and shear modulus G decrease with applied pressure increasing. The other elastic constants and elastic moduli increase with the increasing pressure. Compared with the result given in Ref. [13], our result underestimates the lattice constant by less than 0.16%, which is within the general accuracy of DFT using GGA (usually 1%–2%). At 0 GPa, the bulk modulus of wII-Si₃N₄ is in comparable with that of the α ($B=235.5$ GPa^[21]) and β phases ($B=240$ GPa^[22]). It is well known that for a cubic lattice, the mechanical stability requires the elastic constants satisfying the Borns stability criteria^[23]

$$C_{44} > 0, \quad C_{11} > |C_{12}|, \quad C_{11} + 2C_{12} > 0 \quad (5)$$

The elastic strain, which is used in our elastic constants calculations, is defined in Euler notation^[24]. Therefore, the simple Borns criteria without pressure can be used to judge the elastic stability of our system. From Table 1, we can see that the elastic constants satisfy Eq. (5). This means that the wII phase can retain its mechanical stability in the range of 0–40 GPa. Unfortunately, there are no experimental data or theoretical results for us to compare with.

In Table 2, the lattice parameters and elastic constants of the post-spinel phase are clearly seen. The lattice constants b and c are in good agreement with

Table 1 Lattice parameters, elastic constants and elastic moduli of wII-Si₃N₄ at different pressures

Pressure / GPa	a /nm	C_{11} /GPa	C_{12} /GPa	C_{44} /GPa	B /GPa	G /GPa	VASP ^[13]
0	0.6465	374.7	190.5	213.6	251.9	153.8	$a=0.6475$ nm
10	0.6386	403.4	230.5	225.5	288.2	153.6	–
20	0.6316	427.5	267.2	234.5	320.6	152.6	–
30	0.6253	422.2	299.8	242.7	347.3	148.8	–
40	0.6195	452.9	329.5	249.0	370.7	143.3	–

the results shown in Ref. [14]. The elastic constants and elastic moduli are very high, which indicates that post-spinel Si_3N_4 belongs to super-hard materials. The Born's criteria for the orthorhombic system are^[25,26]

$$\begin{aligned} C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) &> 0, \\ C_{ii} &> 0, \\ (C_{11} + C_{22} - 2C_{12}) &> 0, \\ (C_{11} + C_{33} - 2C_{13}) &> 0, \\ (C_{22} + C_{33} - 2C_{23}) &> 0, \end{aligned} \quad (6)$$

The elastic constants listed in Table 2 satisfy Eq. (6), which means that post-spinel Si_3N_4 can retain its stability in the pressure range of 160–240 GPa. It is worth noting that the elastic constants C_{11} , C_{12} , C_{13} and C_{44} of post-spinel Si_3N_4 (at 0 GPa) are negative, which indicates that the post-spinel Si_3N_4 compound could not exist at 0 GPa.

The computed lattice constant a ($a=0.8899$ nm) is not in agreement with the result shown in Ref. [14] ($a=0.2660$ nm). During the modeling process, we found that more than 1/4 atoms in the unit cell colliding with each other if $a=0.2660$ nm^[15]. Generally speaking, first-principles calculations using GGA-PBE usually overestimates the lattice constants by less than 5%. Such a big difference may be ascribed to the different cells used in this paper (crystallographic cell) and in Ref. [14] (primitive cell with 1/4 volume of the crystallographic cell). The lattice parameters and elastic constants of β - and γ - Si_3N_4 have been thoroughly discussed and compared with other results in our previous publications^[21,22] and a good agreement was found. Therefore, the lattice parameters and elastic constants of β - and γ - Si_3N_4 are ignored in this paper. Considering the fact that our calculated lattice constants for β -, γ - and wII- Si_3N_4 are correct^[21,22],

we believe that the calculated lattice constants for post-spinel Si_3N_4 are correct too.

3.2 Phase transitions

As a well-known fact, the pressure P_t , at which Gibbs free energies of the two phases are the same, is the critical transition pressure. As shown in Fig. 1(a), we have calculated the Gibbs free energies of wII- and β - Si_3N_4 as functions of pressure. The thermodynamic rule, for the equal Gibbs free energy, at the critical point, suggests that the transition pressure of the $\beta \rightarrow$ wII transformation is 20.8 GPa (at 300 K). This is in consistence with Kroll's result (20 GPa at 0 K)^[13]. At low pressures, β - Si_3N_4 is more stable since $G_\beta < G_{\text{wII}}$. When $P > 20.8$ GPa, the wII phase is more energy favorable. The transition pressure obtained, P_t , as a function of temperature, is plotted in Fig. 1(b). The curve increases rapidly with applied pressure increasing, then it gradually approaches to a linear increase when $P > 21$ GPa.

The Gibbs free energy difference $G_{\text{ps}} - G_\gamma$ is plotted in Fig. 1(c). The calculation shows that Si_3N_4 will undergo a phase transition from the γ phase to the post-spinel phase with the increasing pressure. The transition pressures are determined to be 152.1, 152.5, 155.3, 161.6, 170.3 and 181.8 GPa at temperatures of 0, 300, 600, 900, 1200 and 1500 K, respectively. When $G_{\text{ps}} - G_\gamma = 0$, the corresponding P_t is 152.5 GPa (at 300 K). Our result is in agreement with Kroll's result (160 GPa at 0 K)^[14], but not in agreement with Tatsumis result ($P_t=210$ GPa at 0 K)^[5]. Experimental investigations may be required to evaluate the transition pressures between γ - Si_3N_4 and post-spinel Si_3N_4 with higher reliability.

Fig. 1(d) shows the phase boundary of $\gamma \rightarrow$ post-spinel transformation. The transition curve increases rapidly with applied pressure increasing in the low pressure region ($P < 154$ GPa) and then increases linearly and moderately with the increasing pressure. The transition pressure of $\gamma \rightarrow$ post-spinel transition

Table 2 Lattice parameters, elastic constants and elastic moduli of post-spinel Si_3N_4 at different pressures

Pressure / GPa	a/nm	b/nm	c/nm	B/GPa	G/GPa	C_{11}/GPa	C_{12}/GPa
0	0.2660 ^[14]	0.8910 ^[14]	0.9180 ^[14]	–	–	–	–
0	0.8899	0.9180	0.7985	–	–	–	–
160	0.8054	0.8283	0.7258	852.1	414.7	1520.5	566.1
200	0.7933	0.8162	0.7157	974.8	470.2	1736.9	670.4
240	0.7827	0.8057	0.7069	1094.9	520.9	1944.4	776.3
	C_{13}/GPa	C_{22}/GPa	C_{23}/GPa	C_{33}/GPa	C_{44}/GPa	C_{55}/GPa	C_{66}/GPa
160	458.2	1452.1	668.9	1328.7	383.4	582.4	299.1
200	513.5	1633.2	756.4	1542.0	446.9	624.9	345.9
240	566.3	1810.5	842.2	1749.6	498.8	664.1	391.2

is much higher than that of $\beta \rightarrow \text{wII}$ transition. The phase boundaries can be written as

$$P = 18.6221 - 2.24 \times 10^{-3}T + 4.14975 \times 10^{-5}T^2 - 3.08314 \times 10^{-8}T^3 + 7.91965 \times 10^{-12}T^4, (\beta \rightarrow \text{wII}) \quad (7)$$

$$P = 152.26245 - 4.06 \times 10^{-3}T + 1.23362 \times 10^{-5}T^2 + 6.34838 \times 10^{-9}T^3 - 2.76267 \times 10^{-12}T^4, (\gamma \rightarrow \text{post-spinel}) \quad (8)$$

To the authors knowledge, there are no experimental data or theoretical results available related to the $\beta \rightarrow \text{wII}$ and $\gamma \rightarrow \text{post-spinel}$ phase boundaries in the literatures for us to compare with. Our paper is the first attempt in this direction.

3.3 Thermodynamics properties

Using the quasi-harmonic Debye approximation, we have also obtained the bulk modulus of Si_3N_4 .

The isothermal bulk modulus B_T can be defined as the volume derivatives of pressure. Knowledge of B_T is necessary for understanding the thermoelastic and anharmonic properties of solids^[27,28]. We show in Fig. 2 the thermal effects on the isothermal bulk modulus B_T and adiabatic bulk modulus B_S of

wII- and post-spinel Si_3N_4 . In Fig. 2(a), B_S is nearly unchanged between 0 and 300 K and then decreases moderately with applied temperature increasing. When $T < 200$ K, B_T is almost a constant too, then it decreases linearly when $T > 200$ K. B_T decreases faster than B_S . It is the rapid cell volume variation that makes the bulk modulus decreases. More importantly, the temperature effects on B_T and B_S are significant especially at high temperatures.

B_T shown in Fig. 2(b) is similar to the bulk modulus B_T plotted in Fig. 2(a). B_S increases with the increasing temperature first, then it decreases slowly when $T > 500$ K. The bulk modulus of wII- Si_3N_4 decreases more rapidly than that of post-spinel Si_3N_4 , which indicates that wII- Si_3N_4 is more compressible at high temperature. Because $B_S = B_T (1 + \alpha\gamma T)$, B_T and B_S coincide at zero temperature and diverge more and more when T increases. At 0 K, the calculated bulk moduli B_T are 252.3 (at 0 GPa) and 858.4 GPa (at 160 GPa) for wII- and post-spinel Si_3N_4 , respectively. The data listed in Tables 1 and 2 are in agreement with the bulk moduli obtained by the elastic constants for wII- ($B=251.9$ GPa at 0 GPa) and post-spinel Si_3N_4 ($B=852.1$ GPa at 160 GPa). The agreement between the Debye bulk modulus and the PW-PP bulk modulus had partially proven the validity and reliability of our calculation.

Fig. 1 (a) Gibbs free energies of the Si_3N_4 polymorphs at 300 K; (b) T-P phase diagram of the β - and wII- Si_3N_4 polymorphs; (c) Gibbs free energy difference of γ - and post-spinel Si_3N_4 at 300 K; (d) the phase boundary between γ - and post-spinel Si_3N_4

Knowledge of the isobaric heat capacity C_p and its temperature dependence not only provides essential insight into the vibrational properties but is also mandatory for many practical applications. As C_p and thermal expansion coefficient α have anharmonic behaviors, we would not expect linear variations with temperature. Fig. 3(a) shows the predicted heat capacities for the wII phase at 0, 10, 20, 30 and 40 GPa, respectively. C_p indicates a sharp increase up to 500 K, which is due mainly to the anharmonic effects of the Debye approximation used here. However, at sufficiently high temperatures, the anharmonic effects are suppressed, and C_p increases linearly with increasing temperature. At a given temperature, C_p decreases with increasing applied pressure.

In Fig. 3(b), it is clearly seen that when $T < 700$ K, the heat capacity is depending on both temperature and pressure. At high temperatures ($T > 700$ K), the temperature effects are more significant than the pressure effects. C_p tends to a constant value at high pressure and high temperature. Unlike the constant volume heat capacity (C_V), C_p follows on a linear increase at high temperatures while C_V approaches to a constant value (Dulong-Petit's limit)^[29]. At 300 K, the calculated heat capacities (C_p) of wII- and post-spinel Si_3N_4 are 113.9 J/(mol·K) (at 0 GPa)

and 25.6 J/(mol·K) (at 160 GPa), respectively. These results need to be verified by experiments in the future.

In Fig. 4, we present the temperature and pressure dependences of volume thermal expansion coefficient α . In Fig. 4(a), α decreases with applied pressure first, then it decreases slowly between 16–32 GPa, and above 16 GPa the curves arrive to linear regimes. At a given temperature, α decreases rapidly with the increasing pressure. At a certain pressure, α increases with increasing applied temperature. These results are in accordance with the fact that the effect of increasing pressure on a material is just the same as decreasing its temperature. As shown in Fig. 4(b), the pressure effect on the thermal expansion coefficient of post-spinel Si_3N_4 is nearly linear. The higher the temperature is, the faster the thermal expansion decreases. The effects of temperature on α are larger than the pressure effects on α . At 300 K, the calculated thermal expansion coefficients for wII- and post-spinel Si_3N_4 are 8.9×10^{-6} /K (at 0 GPa) and 0.3×10^{-6} /K (at 160 GPa), respectively. This work is a first attempt on the phase transition character, heat capacity and thermal expansion of wII- and post-spinel Si_3N_4 . Thus, our results can serve as a prediction for future study of Si_3N_4 .

Fig. 2 Bulk modulus *vs.* temperature diagrams of wII- Si_3N_4 at 0 GPa (a) and post-spinel Si_3N_4 at 160 GPa (b)

Fig. 3 Predicted heat capacity C_p *vs.* temperatures and pressures of wII- Si_3N_4 (a) and post-spinel Si_3N_4 (b)

Fig. 4 Predicted thermal expansion coefficient α vs. temperatures and pressures of wII-Si₃N₄ (a) and post-spinel Si₃N₄ (b)

4. Conclusions

(1) β -Si₃N₄ is predicted to undergo a structural phase transition to the wII phase at 20.8 GPa and 300 K. The critical pressure of the first-order $\gamma \rightarrow$ post-spinel transformation is 152.5 GPa (at 300 K) and it increases to 181.8 GPa at 1500 K. Besides, the phase boundaries of the $\beta \rightarrow$ wII and $\gamma \rightarrow$ post-spinel transitions are also successfully obtained. Both boundaries have positive slopes.

(2) The ground-state lattice parameter, elastic constant, bulk modulus and shear modulus of wII- and post-spinel Si₃N₄ are investigated. Using the quasi-harmonic approximation, thermal expansion, some fundamental properties like bulk modulus and heat capacity are calculated as functions of pressure and temperature. Some interesting features are found in these quantities.

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