Theoretical Study on the High-Temperature $P6\bar{6}$ and $P6'\bar{6}$ Phases of Si$_3$N$_4$: A Tool to Aid in Ceramics Development

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(Dated: Received on August 15, 2013; Accepted on October 14, 2013)

Atomistic modeling based on the density functional theory combined with the quasi-harmonic approximation is used to investigate the lattice parameters and elastic moduli of the $P6$ and $P6'$ phases of Si$_3$N$_4$. $\beta$-Si$_3$N$_4$ is set as a benchmark system since accurate experiments are available. The calculated lattice constants and elastic constants of $\beta$-Si$_3$N$_4$ are in good agreement with the experimental data. The crystal anisotropy, mechanical stability, and brittle behavior of $P6$- and $P6'$-Si$_3$N$_4$ are also discussed in the pressure range of 30–55 GPa. The results show that these two polymorphs are metallic compounds. The brittleness and elastic anisotropy increase with applied pressure increasing. Besides, the phase boundaries of the $\beta\rightarrow P6'\rightarrow \delta$ transitions are also analysed. The $\beta$ phase is predicted to undergo a phase transition to the $P6'$ phase at 40.0 GPa and 300 K. Upon further compression, the $P6'\rightarrow \delta$ transition can be observed at 53.2 GPa. The thermal and pressure effects on the heat capacity, cell volume and bulk modulus are also determined. Some interesting features are found at high temperatures.

Key words: First-principles, Nitrides, Brittleness, Phase diagram

I. INTRODUCTION

Silicon nitride (Si$_3$N$_4$) belongs to the group-IV nitrides exhibiting unique physical properties. As an important ceramic, Si$_3$N$_4$ can be used as gas turbines, cutting tools, etch masks, solar cells, and energy conversion materials [1, 2]. Its low density, high strength, tunable electrical conductivity and high decomposition temperature lead to numerous applications [1, 3]. There are several Si$_3$N$_4$ polymorphs, namely $\alpha$ phase (space group: $P3_1c$) [4], $\beta$ phase (space group: $P6_3/m$) [4], willemite-II phase (wll-Si$_3$N$_4$, space group: $I43d$) [5], $\gamma$ phase (space group: $Fd\bar{3}m$) [6], $\delta$ phase (space group: $P3$) [7], and post-spinel phase (space group: BBMM) [8]. In recent years, the $\alpha\rightarrow \beta$ [9, 10], $\beta\rightarrow$ wll [5], $\beta\rightarrow \gamma$ [7, 11–13], $\alpha\rightarrow \gamma$ [7], $\beta\rightarrow \delta$ [7], and $\gamma\rightarrow$ post-spinel [8, 14] phase transitions have been carefully investigated.

Xu et al. found new Si$_3$N$_4$ polymorphs (the hexagonal $P6$ and $P6'$ phases, space group: $P3$), and observed the high-pressure $\beta\rightarrow P6'\rightarrow \delta$ phase transitions [7]. Although many efforts have been made on Si$_3$N$_4$, the $P6$ and $P6'$ phases are far less studied than their counterparts $\alpha$, $\beta$, wll, $\delta$, and $\gamma$-Si$_3$N$_4$. Due to the difficulties in the preparation of polycrystalline samples [7], theoretical calculations, especially first-principles method, can help. Using first-principles calculation, we provide predictions of the thermal quantities, elastic properties, phase stabilities, and phase transition characters of the $\beta$, $P6$, $P6'$, and $\delta$ phases.

II. BENCHMARK CALCULATION

Present calculations are performed using the first-principles plane-wave method [15] in combination with ultrasoft pseudo-potentials (US-PP) [16] to calculate the total energy of Si$_3$N$_4$. The Perdew-Burke-Ernzerhof functional [17] is used for the exchange-correlation potential. In consideration of accuracy, the plane-wave cut off energies of 500 eV ($\beta$-Si$_3$N$_4$), 450 eV ($P6$-Si$_3$N$_4$), 450 eV ($P6'$-Si$_3$N$_4$), and 450 eV ($\delta$-Si$_3$N$_4$) are used in our calculation. The $k$-point meshes, based on the Monkhorst-Pack scheme [18], are 4×4×12 for $\beta$-Si$_3$N$_4$, 5×5×12 for $P6$-Si$_3$N$_4$, 5×5×12 for $P6'$-Si$_3$N$_4$, and 6×6×15 for $\delta$-Si$_3$N$_4$, respectively. The internal coordinates of different atoms have been fully relaxed. Reference configurations for the valence electrons are Si$s^2$p$^2$ and N$s^2$p$^3$. The calculated total energies of Si$_3$N$_4$ are converged to less than 1 µeV/atom. Besides, the crystal structures and atomic coordinates of $P6$- and $P6'$-Si$_3$N$_4$ can be found in Ref.[7].

The $k$-point mesh should be described in order to avoid the unclearness. In fact, the $k$-points are determined by the equation $(1/a_1/b_1/c_1)$, where $a$, $b$, and $c$ are the lattice constants. For $\beta$-Si$_3$N$_4$, the experimental values of the lattice constants are $a=b=0.7607$ nm and $c=0.2907$ nm (see Table I), thus $1/a_1/b_1/c_1 \approx 1:2:62$. The $k$-point mesh can be chosen as $3\times 3\times 8$, $4\times 4\times 12$, $5\times 5\times 12$, and $6\times 6\times 15$. The calculated lattice constants and elastic constants of $\beta$-Si$_3$N$_4$ and $P6$-Si$_3$N$_4$ are in good agreement with the experimental data.
5×5×14, etc. According to our convergence tests, the plane-wave cutoff 500 eV and the k-points 4×4×12 can generate good results for β-Si$_3$N$_4$. For the hexagonal P6- and P6'-Si$_3$N$_4$, we do not know the experimental lattice constants. The only known parameters are the internal coordinates of atoms [7]. We have built the unit cell for P6'-Si$_3$N$_4$ using $a=b=1.0$ nm and $c=0.5$ nm. After geometry optimization and full relaxation of internal coordinates with very high cut-off energy and k-points, the equilibrium lattice constants can be obtained. According to the equation (1/a:1/b:1/c) and the convergence tests, the adequate parameters for P6'- and P6-Si$_3$N$_4$ are found to be cut-off energy of 450 eV and k-points 5×5×12.

Then, we apply the quasi-harmonic approximation (QHA) scheme [19, 20], in which the non-equilibrium Gibbs function $G^*(V;P,T)$ can be determined by

$$G^*(V;P,T) = E(V) + pV + A_{vib}(V;T)$$

where $E(V)$ is the total energy, $pV$ represents the hydrostatic pressure condition, $A_{vib}$ is the vibrational term, which can be written as [21]:

$$A_{vib}(\theta_D;T) = nkT\left\{\frac{9\theta_D^2}{8T} + 3\ln\left[1 - \exp\left(-\frac{\theta_D}{T}\right)\right] - D\left(\frac{\theta_D}{T}\right)\right\}$$

where $n$, $\theta_D$, $T$, and $D(\theta_D/T)$ are the number of atoms, the Debye temperature, the temperature and the Debye integral, respectively. Accordingly, $G^*(V;P,T)$ can be minimized by

$$\left[\frac{\partial G^*(V;p,T)}{\partial V}\right]_{p,T} = 0$$

By solving Eq.(3), some thermal properties such as constant-volume heat capacity ($C_V$), isobaric heat capacity ($C_P$) and isothermal bulk modulus ($B_T$) can be obtained by

$$C_V = 3nk_b\left[4D\left(\frac{\theta_D}{T}\right) - \frac{3\theta_D}{T}\exp(\theta_D/T) - 1\right]$$

$$C_P = C_V(1+\alpha\gamma T)$$

$$B_T = -\frac{1}{x^2}B_0\exp\left(\frac{p - p_{sp}}{0.15}\right)$$

where $p_0$ is the equilibrium volume, $k_B$ the Boltzmann’s constant, $\alpha$ the thermal expansion coefficient, $B_0$ the zero-pressure bulk modulus, $\gamma$ the Grüneisen parameter, $p_{sp}$ the spinodal pressure, $L^*$ the fitting parameter, and $B_0'$ is the first-order derivative of $B_0$, respectively.

A detailed expression of QHA can be found in Refs. [19, 20].

III. RESULTS AND DISCUSSION

The experimentally confirmed and theoretically hypothesized transition paths of the Si$_3$N$_4$ polymorphs are illustrated in Fig.1. The $\beta\rightarrow$P6→δ transitions have not been verified by experiments or theoretical studies. In order to have a deep insight into the fundamental properties of Si$_3$N$_4$, we have calculated the pressure dependences of lattice constants, cell volumes, elastic constants, and elastic moduli. The results are shown in Tables I and II.

Since the experimental data of $\beta$-Si$_3$N$_4$ are available, we have calculated the fundamental properties of the
TABLE II Calculated elastic constants $C_{ij}$ (in GPa), bulk modulus $B_H$ (in GPa), shear modulus $G_H$ (in GPa), Young’s modulus $Y_H$ (in GPa), Poisson ratio $\sigma$ and anisotropy factor $A$ of $\bar{P}^\prime_6$- and $\bar{P}^{6'}_6$-$\text{Si}_3\text{N}_4$.

<table>
<thead>
<tr>
<th>P/GPa</th>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$B_H$</th>
<th>$G_H$</th>
<th>$B_H/G_H$</th>
<th>$Y_H$</th>
<th>$\sigma$</th>
<th>$A$</th>
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<td>198.9</td>
<td>490.7</td>
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<td>211.8</td>
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$\beta$ phase. As shown in Table I, the predicted lattice constants and cell volumes are in excellent agreement with the experimental data and the theoretical results. The calculated elastic constants of $\beta$-$\text{Si}_3\text{N}_4$ given in our previous work [10] were also in satisfactory agreement with the results in Refs. [7, 22]. For $\bar{P}^\prime_6$- and $\bar{P}^{6'}_6$-$\text{Si}_3\text{N}_4$, $a$, $c$, and $V$ decrease with the pressure increasing. The cell volume of the $\bar{P}^\prime_6$ phase is larger than that of the $\bar{P}^{6'}_6$ phase. Therefore, the channels in the $\bar{P}^{6'}_6$ phase are larger than those in $\bar{P}^\prime_6$-$\text{Si}_3\text{N}_4$.

It is well known that the elastic constants are calculated by means of Taylor expansion of the total energy, $E(V, \delta)$, for the system with respect to a small strain $\delta$ of the cell volume $V$. The energy of a strained system can be expressed as follows [28]:

$$E(V, \delta) = E(V_0, T) + V_0 \left( \sum \tau_i \xi_i \delta_i + \frac{1}{2} \sum C_{ij} \tau_i \tau_j \delta_i \right)$$  \hspace{1cm} (11)

where, $E(V_0, T)$ is the energy of the unstrained system with equilibrium volume $V_0$ at different temperatures, $\tau_i$ is an element in the stress tensor, and $\xi_i$ is a factor to consider Voigt index [28]. The total energy $E(V_0, T)$ at a certain temperature $T$ and the finite temperature lattice constant can be obtained by the vibrational Debye-like model. According to the Voigt-Reuss-Hill approximation, the bulk modulus $B_H$, shear modulus $G_H$, Young’s modulus $Y_H$, Poisson ratio $\sigma$ and anisotropy factor $A$ can be obtained by [29]

$$B_H = \frac{1}{2} (B_V + B_R)$$  \hspace{1cm} (12)

$$G_H = \frac{1}{2} (G_V + G_R)$$  \hspace{1cm} (13)

$$Y_H = \left(3B_HG_H - 2B_H^2\right) / 3B_H$$  \hspace{1cm} (14)

$$\sigma = \frac{1}{2} \frac{3B_H - 2G_H}{3B_H + G_H}$$  \hspace{1cm} (15)

$$A = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}}$$  \hspace{1cm} (16)

where the subscripts $V$, $R$, and $H$ are the Voigt index, the Reuss index, and the Hill index, respectively. These quantities are listed in Table II.

For a hexagonal lattice, there are five independent elastic constants $C_{11}$, $C_{12}$, $C_{13}$, $C_{33}$, and $C_{44}$ ($2C_{66}=C_{11}-C_{12}$). As listed in Table II, the elastic constants $C_{ij}$, elastic moduli $B_H$, $G_H$, and $Y_H$ of $\bar{P}^\prime_6$-$\text{Si}_3\text{N}_4$ increase monotonously with applied pressure, but the slopes are different. The pressure effect on $C_{11}$ is significant. The decrease of $C_{14}$ reflects the shear resistance decreases in the {010} or {100} plane in the {001} direction. The value of the Poisson ratio $\sigma$ for cermet materials is quite small (about 0.1), whereas for metallic materials a typical $\sigma = 0.33$ [30]. The calculated $\sigma = 0.320-0.336$, showing moderate lateral expansion when compressed. The $\bar{P}^{6'}_6$ phase is a metallic compound in the whole pressure range of 30–55 GPa. The anisotropy factor $A=1$ represents completely elastic isotropy while any value smaller or larger than 1 indicates elastic anisotropy. $A$ increases as the pressure increases first, then the elastic anisotropy of $\bar{P}^\prime_6$-$\text{Si}_3\text{N}_4$ is quite small at 40 GPa. When $P>40$ GPa, $A$ will gradually strengthen with the pressure increasing. Besides, the $B_H/G_H$ ratio reflects the brittle and ductile behaviors of polycrystalline materials since solids behave in brittle manners if $B_H/G_H$$>2$ [31]. $\bar{P}^{6'}_6$-$\text{Si}_3\text{N}_4$ remains brittle in the pressure range of 30–55 GPa. The brittleness increases with the pressure increasing. More importantly, the chemical bonds in $\bar{P}^{6'}_6$-$\text{Si}_3\text{N}_4$ are ionic due to the fact that the typical $B/G$ ratios for covalent and ionic solids are 0.91 and 1.67, respectively.

In Table II, we can see that the elastic moduli of $\bar{P}^\prime_6$-$\text{Si}_3\text{N}_4$ do not follow the same trend. $C_{12}$, $C_{13}$, and $B_H$ increase with the increasing pressure whereas $G_H$ and $Y_H$ show the opposite trends. $C_{11}$, $C_{33}$, and $C_{44}$ increase first, and then decrease with the increasing pressure. The calculated $\sigma = 0.347-0.399$, which indicates that $\bar{P}^\prime_6$-$\text{Si}_3\text{N}_4$ is a metallic compound. The variation of $A$ with pressure ($\bar{P}^\prime_6$-$\text{Si}_3\text{N}_4$) is similar to that
of $P6\text{-}Si_3N_4$. The anisotropy of $P6\text{-}Si_3N_4$ is stronger than that of $P6\text{'}\text{-}Si_3N_4$ since $|A(P6\text{'}\text{-})|<|A(P6\text{-})|$. According to the $B_{ii}/G_{ii}$ ratio, $P6\text{-}Si_3N_4$ is more brittle than $P6\text{'}\text{-}Si_3N_4$. For a hexagonal structure, the mechanical stability can be determined by the Born’s criteria [32]: $C_{11}-|C_{12}|>0$, $C_{44}>0$, $(C_{11}+C_{12})C_{33}-2C_{13}^2>0$. At 0 K, $P6\text{-}$ and $P6\text{'}\text{-}Si_3N_4$ are stable in the pressure range of 30–55 GPa since all the elastic constants satisfy these criteria. Besides, the bulk moduli of the two phases are greater than the bulk moduli of $\alpha$, $\beta$, and $\gamma$ phases [33].

The transition pressures among different phases of solids can be obtained by comparing the Gibbs free energy $G$ of different phases. We have calculated the Gibbs free energy difference between $\beta\text{-}Si_3N_4$ and $P6\text{'}\text{-}Si_3N_4$, as shown in Fig.2(a). The thermodynamic requirement, for the equality of $G$, at the critical points, suggests that the transition pressures of the $\beta\rightarrow P6\text{'}$ transition are 40.0, 42.7, and 46.2 GPa at temperatures of 300, 500, and 700 K, respectively. $\beta\text{-}Si_3N_4$ has the lower free energy at low pressures, which indicates that this phase is the low-temperature phase of $Si_3N_4$. The Gibbs free energy difference obtained, $G_{\beta\rightarrow P6\text{'}}/G_{P6\text{-}}$, as a function of pressure is given in Fig.2(b). It is clearly seen that the transition pressure between the $P6\text{-}$ phase and the $\delta$ phase is 53.2 GPa (at 300 K), at which the $P6\text{-}$ phase will automatically transform into $\delta\text{-}Si_3N_4$. $P6\text{'}\text{-}Si_3N_4$ has the lower free energies when $P<53.2$ GPa. The $\delta$ phase has the lower free energies at higher pressure, i.e. $\delta\text{-}Si_3N_4$ would be favored at sufficiently high pressures. The $\delta$ phase boundaries of the $\beta\rightarrow P6\text{'}\rightarrow \delta$ transitions are illustrated in Fig.2(c).

As shown in Fig.2(c), the slopes of the $\beta\rightarrow P6\text{'}$ and $P6\text{'}\rightarrow \delta$ transitions are both positive, which suggests that at higher temperatures it will require higher pressures to synthesize $P6\text{'}\text{-}Si_3N_4/\delta\text{-}Si_3N_4$. It is found that the transition pressure from the $\beta$ phase to the $P6\text{-}$ phase is 40.0 GPa (at 300 K). The critical pressure of the $\beta\rightarrow P6\text{'}$ transition is about 13 GPa higher than that of the $P6\text{'}\rightarrow \delta$ transition. According to the Clausius-Clapeyron relation [11], the slope of the phase boundary can be determined by $\Delta S/\Delta V$, where $\Delta S$ and $\Delta V$ are the entropy change and the volume variation, respectively. Therefore, the $\beta\rightarrow P6\text{'}\rightarrow \delta$ transitions are accompanied by the shrinkage of volume, which is in agreement with the cell volumes listed in Table I (the calculated volume of $\delta\text{-}Si_3N_4$ at 55 GPa is 109.6 Å$^3$).

One of the most important vibrational properties of solids is the temperature dependence of heat capacity. Figure 3 (a) and (b) give the evolutions of the constant-pressure heat capacity $C_p$ with temperature for $P6\text{-}$ and $P6\text{'}\text{-}Si_3N_4$, respectively. As shown in Fig.3(a), $C_p$ is very small at low temperature. From 0 to 500 K, $C_p$ increases exponentially with the temperature increasing. At high temperatures, $C_p$ follows a linear increase, which is not similar to the constant-volume heat capacity $C_V$ ($C_V$ follows the Dulong-Petit’s law, i.e. 3R for monoatomic solids). Although $C_V$ gives direct information on the intrinsic anharmonic effects, it is $C_p$ that is experimentally measured, and it contains both anharmonic effects and quasi-harmonic contributions. In Fig.3(b), it is clearly seen that $C_p$ increases rapidly at low temperatures, and reaches a plateau region at high temperatures. The heat capacity of $P6\text{-}Si_3N_4$ is larger than that of $P6\text{'}\text{-}Si_3N_4$ at the same temperature.

In Fig.3(c), it is clearly seen that the volumes of $P6\text{-}$ and $P6\text{'}\text{-}Si_3N_4$ decrease smoothly as pressure increases. The $V/V_0$ ratio of $P6\text{-}Si_3N_4$ decreases faster than that of $P6\text{'}\text{-}Si_3N_4$. At high pressures, the difference between the two curves can be clearly seen. This means that the $P6$ phase is more compressible than the $P6\text{'}$ phase. Figure 3(d) shows the evolutions of bulk moduli with pressure at 300 K. The bulk modulus increases with the increasing pressure but the rate of increase is moderate. The first sticking feature is that the bulk modulus of $P6\text{'}\text{-}Si_3N_4$ is greater than that of $P6\text{-}Si_3N_4$. The second feature is that the slopes of the two curves are different. At 50 GPa and 300 K, the calculated bulk modulus and heat capacity are 391.4 GPa (343.2 GPa) and 44.8 J/(mol K) (77.2 J/(mol K)) for

FIG. 2 (a) Gibbs free energy difference $(G_{P6\text{-}}-G_{\beta})$ as a function of pressure. (b) Critical pressure as a function of Gibbs free energy difference of the $P6\text{-}\rightarrow \delta$ transition at 300 K. (c) Relationships of the transition pressures of the $\beta\rightarrow P6\text{'}\rightarrow \delta$ transitions with temperature.
FIG. 3 The constant-pressure heat capacity $C_P$ (at 50 GPa) for (a) $P\bar{6}$-Si$_3$N$_4$, (b) $P\bar{6}'$-Si$_3$N$_4$, (c) the normalized cell volume $V/V_0$ ($V_0$ is the equilibrium cell volume at 40 GPa), and (d) bulk modulus of Si$_3$N$_4$ at 300 K.

$P\bar{6}'$-Si$_3$N$_4$ ($P\bar{6}$-Si$_3$N$_4$), respectively.

IV. CONCLUSION

First-principles calculations are carried out on Si$_3$N$_4$ in the recently-discovered $P\bar{6}'$ and $P\bar{6}$ phases to investigate their stability and physical properties, which have not yet been established experimentally. As a benchmark system ($\beta$-Si$_3$N$_4$), the calculated lattice constants and elastic moduli are in agreement with the experimental data. The lattice parameters, cell volume, elastic constants, elastic moduli, anisotropy factor and Poisson ratio of $P\bar{6}$- and $P\bar{6}'$-Si$_3$N$_4$ are also predicted in the pressure range of 30–55 GPa. $\beta$-Si$_3$N$_4$ is predicted to undergo a first-order phase transition to the $P\bar{6}'$ phase at 40.0 GPa and 300 K. Upon further compression, the $P\bar{6}'\rightarrow\delta$ transformation can be observed at 53.2 GPa. The positive slopes of the $\beta\rightarrow P\bar{6}'\rightarrow\delta$ transitions mean that the two phase transformations are accompanied by the shrinkage of volume. The two polymorphs are brittle compounds with little metallic character, which is not similar to the $\beta$ phase. The anisotropy of $P\bar{6}'$-Si$_3$N$_4$ increases with the increasing pressure while the anisotropy of $P\bar{6}$-Si$_3$N$_4$ shows the opposite trend. The heat capacity increases rapidly at low pressures, and reaches a plateau at high pressures. Furthermore, the $P\bar{6}$ phase is more compressible than the $P\bar{6}'$ phase.

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.U1204501, No.11105115, and No.11304141), the Project of Basic and Advanced Technology of Henan Province of China (No.112300410021), and the Key Project of Henan Educational Committee (No.12A140010). The authors are grateful to Prof. M. A. Blanco from the Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo for the Gibbs code.


DOI:10.1063/1674-0068/27/01/103-108 ©2014 Chinese Physical Society