

# Structural, Mechanical, and Thermal Properties of $\beta$ - $\text{Si}_3\text{N}_4$ under High Pressure

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**Abstract** Intensive calculations have been carried out to study the structural, mechanical, and thermal properties of  $\beta$ - $\text{Si}_3\text{N}_4$  with hexagonal P63/m structure. The calculated lattice constants  $a$  and  $c$  are in agreement with the available experimental data and similar theoretical calculations. Through a series of researches, the mechanical parameters (the elastic constants, bulk modulus, shear modulus, and Young's modulus) and Debye temperature, the wave velocities are systematically investigated. Additionally, the mechanical anisotropy has been characterized by calculating Young's modulus and described by the three-dimensional (3D) surface constructions and its projections. By using the born stability criteria and phonon frequency, it is concluded that the  $\beta$ - $\text{Si}_3\text{N}_4$  is stable mechanically and dynamically up to 35 GPa. Finally, the thermal properties have been calculated by employing the quasi-harmonic Debye model at different temperatures (0–800 K) and pressures (0–35 GPa).

**Keywords**  $\beta$ - $\text{Si}_3\text{N}_4$  · Elastic · Thermal properties

## 1 Introduction

$\text{Si}_3\text{N}_4$  is widely used as an important ceramic with many industrial applications, such as under high temperature

and corrosive environments. Three polymorphs for  $\text{Si}_3\text{N}_4$  exist:  $\alpha$ - $\text{Si}_3\text{N}_4$ ,  $\beta$ - $\text{Si}_3\text{N}_4$ , and  $\gamma$ - $\text{Si}_3\text{N}_4$ . Both  $\alpha$ - $\text{Si}_3\text{N}_4$  and  $\beta$ - $\text{Si}_3\text{N}_4$  have hexagonal structures P31/c and P63/m and can be produced at ambient conditions [1, 2].  $\gamma$ - $\text{Si}_3\text{N}_4$  has a cubic structure. It can be produced at temperatures above 2000 K and pressures above 15 GPa [3, 4]. It is found that  $\beta$ - $\text{Si}_3\text{N}_4$  is a more stable phase [5]. Recently, Cui et al. have predicted three potential hard metastable phases of t- $\text{Si}_3\text{N}_4$ , m- $\text{Si}_3\text{N}_4$ , and o- $\text{Si}_3\text{N}_4$  using a recently developed particle swarm optimization method within the CALYPSO software package [6]. In this paper, we focus on the  $\beta$ - $\text{Si}_3\text{N}_4$ . In recent years, frequent experimental and theoretical attempts have been used to study the  $\beta$ - $\text{Si}_3\text{N}_4$  [7–14]. On the experimental side, Flammini et al. have carried out the thermal oxidation of the  $\beta$ - $\text{Si}_3\text{N}_4$  (0001)- $8 \times 8$  surface [10]. On the theoretical side, Ching et al. have optimized the experimentally observed phases of  $\text{Si}_3\text{N}_4$  crystal structures by employing first principles calculation [11]. Kuwabara et al. have calculated the lattice dynamics of  $\alpha$ - $\text{Si}_3\text{N}_4$ ,  $\beta$ - $\text{Si}_3\text{N}_4$ , and  $\gamma$ - $\text{Si}_3\text{N}_4$  phases by interatomic force constants in the real space method combined with first-principles calculations [12]. Lu et al. have performed to clarify the shear mechanical property of  $\beta$ - $\text{Si}_3\text{N}_4$  nano-thin layer in the basal plane with different extreme strain rates and loading temperatures via molecular dynamics simulations [13]. Jiang et al. have also investigated the different roles of Lu and La in the intergranular film in  $\beta$ - $\text{Si}_3\text{N}_4$  on the growth morphology investigated via molecular dynamics simulations [14].

Although there are some studies, the mechanical anisotropy properties of  $\beta$ - $\text{Si}_3\text{N}_4$  are still limited both experimentally and theoretically as far as we are aware. Therefore, we here have extended the mechanical properties and presented the Young's modulus of  $\beta$ - $\text{Si}_3\text{N}_4$  in detail.

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## 2 Methods of Calculation

$\beta$ - $\text{Si}_3\text{N}_4$  crystallize in the hexagonal structure belonging to the space group of P63/m (No. 176). The atomic positions are N 2c (0.3333, 6667, and 0.25), 6h (0.3302, 0.0301, and 0.25), and Si 6h (0.1751, 0.7689, and 0.25). The experimental lattice parameter  $a$  and  $c$  were determined to be 7.6069 and 2.9091 Å from the experimental data [15].

The structure and lattice dynamics of  $\beta$ - $\text{Si}_3\text{N}_4$  calculations are carried out by using the Cambridge Serial Total Energy (CASTEP) code [16], based on density functional theory (DFT) by using Vanderbilt-type ultrasoft pseudopotentials [17] and density functional perturbation theory (DFPT) [18] by using norm-conserving pseudopotential [19], respectively. The effects of exchange-correlation interaction are described with the local density approximation (LDA) of the Ceperley-Alder data as parameterized by Perdew-Zunger (CA-PZ) [20]. Considering accuracy, we choose the cutoff energy to be in 520 eV, and the Brillouin-zone sampling mesh parameters for the  $k$ -point set to be  $7 \times 7 \times 8$  in this work for every calculation. For calculation of the elastic constants, we adopted the same cutoff energy and Monkhorst-Pack mesh as the structure. Through the method described above, Moreira et al. have successfully investigated the elastic properties of some materials [21]. It suggests that the simulation method adopted in this work is reasonable and reliable, giving us confidence in the following calculations.

The thermal properties calculations of  $\beta$ - $\text{Si}_3\text{N}_4$  are carried out by using the quasi-harmonic Debye model [22, 23].

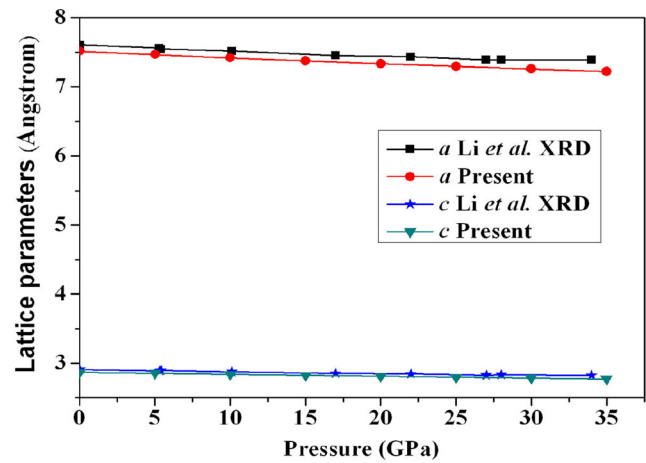
## 3 Results and Discussions

### 3.1 Structural Properties

By performing ab initio density functional calculations using LDA functional within CA-PZ type, we obtained the equilibrium lattice constants for  $a=7.5152$  Å and  $c=2.8702$  Å,

**Table 1** Calculated lattice constants  $a$  (Å),  $c$  (Å), and  $c/a$  of  $\beta$ - $\text{Si}_3\text{N}_4$ , together with experimental data and theoretical results

	$a$	$c$	$c/a$
Present work	7.5153	2.8702	0.3819
Exp. [15]	7.6069	2.9091	0.3824
Exp. [24]	7.608	2.90	0.3812
Ref.[8]	7.562	2.893	0.3826
Ref. [11]	7.6226	2.9014	0.3818
Ref. [25]	7.61	2.91	0.3824
Ref. [26]	7.580	2.899	0.3825
Ref. [27]	7.555	2.814	0.3725

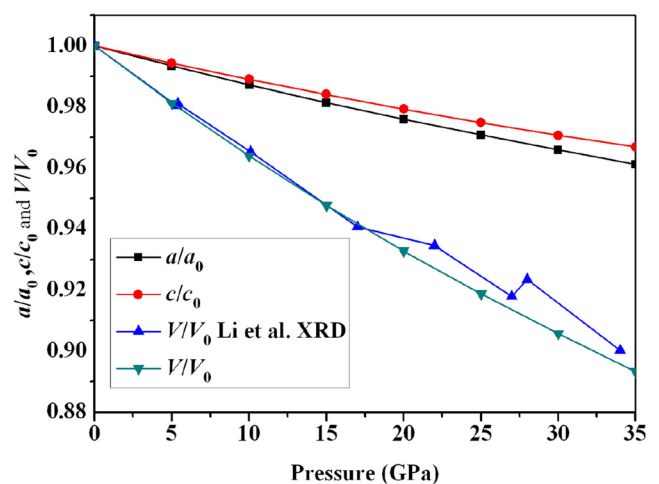


**Fig. 1** The lattice constants  $a$  and  $c$  as a function of pressure at zero temperature

which are very close to the experimental works:  $a=7.6069$  Å and  $c=2.9091$  Å [15, 24] and other theoretical results [8, 11, 25–27]. The above optimized lattice constants are listed in Table 1 together with the available experimental data and theoretical results. Then we further obtained the lattice constants  $a$ ,  $c$  and the relative lattice constants  $a/a_0$ ,  $c/c_0$ , and relative volume  $V/V_0$  as a function of the applied pressure are given in Figs. 1 and 2, respectively, along with Li et al. XRD experimental data [11]. We found that present calculated values are consistent with Li et al. XRD experimental data. It is also worth seeing that the lattice constants  $a$  of  $\beta$ - $\text{Si}_3\text{N}_4$  decreases more with applied pressure than the lattice constants  $c$  in Fig. 1.

### 3.2 Elastic Properties

For hexagonal P63/m structure, the number of the independent elastic constants reduces to five  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{33}$ , and



**Fig. 2** The relative lattice constants  $a/a_0$ ,  $c/c_0$ , and relative volume  $V/V_0$  as a function of pressure at zero temperature

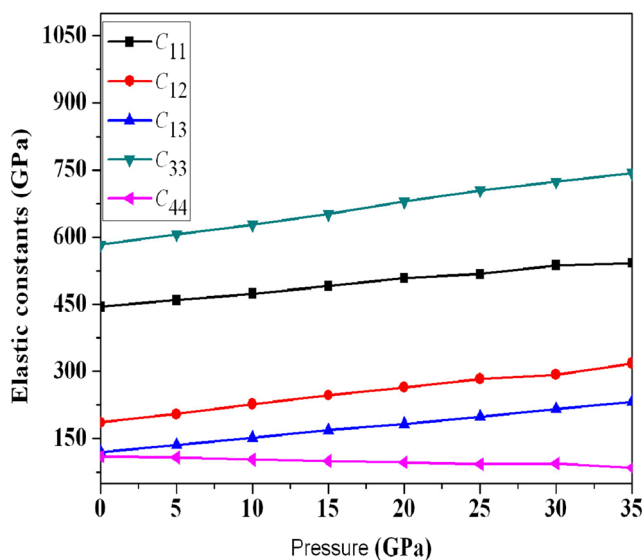
**Table 2** Calculated elastic constants  $C_{ij}$  (GPa) of  $\beta$ - $\text{Si}_3\text{N}_4$  under 0 pressure up to 35 GPa, together with experimental data and theoretical results

Pressure(GPa)	$C_{11}$	$C_{12}$	$C_{13}$	$C_{33}$	$C_{44}$
0	444.96	186.35	119.65	583.27	109.84
0 Expt.	433 [9]	195 [9]	127 [9]	574 [9]	108 [9]
0 Cal.	439.172 [29]	181.848 [29]	149.909 [29]	556.983 [29]	114.380 [29]
0 Cal.	409.3 [30]	271.2 [30]	200.6 [30]	603.6 [30]	108.0 [30]
0 Cal.	343 [31]	136 [31]	120 [31]	600 [31]	124 [31]
0 Cal.	315 [32]	239 [32]	222 [32]	332 [32]	40 [32]
5	459.77	204.83	135.70	606.49	108.18
10	473.88	227.17	151.49	628.41	102.84
15	490.82	246.87	168.50	651.76	100.10
20	508.44	264.53	182.49	680.26	96.67
25	517.41	283.41	198.90	704.70	92.17
30	537.12	292.64	216.10	724.21	93.95
35	541.81	318.40	232.16	743.49	85.25

$C_{44}$ . In order to check the influence of these elastic constants ( $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{33}$  and  $C_{44}$ ) on the mechanical stability, we referred to the Born stability criteria [28]. The calculated elastic constants of  $\beta$ - $\text{Si}_3\text{N}_4$  under 0 pressure and high pressure up to 35 GPa are given in Table 2. From Table 2, we found  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{33}$ , and  $C_{44}$  still obey the Born stability criteria up to 35 GPa, indicating that  $\beta$ - $\text{Si}_3\text{N}_4$  is still mechanically stable up to 35 GPa. The calculated elastic constants of  $\beta$ - $\text{Si}_3\text{N}_4$  under 0 pressure are given in Table 2, and we compared them with experimental data by using Brillouin scattering experimental [9] and other similar theoretical calculations [29–32]. From it, we can find that the present calculated elastic constants are more close to the experimental values [9]. However, our obtained results are also quite consistent with other available calculations obtained by using a force field molecular

dynamics simulation, based on ab initio calculations [29]. In Fig. 3, we also plotted the variation of elastic constants of  $\beta$ - $\text{Si}_3\text{N}_4$  with respect to the variation of pressure. It is found from Fig. 3 that the elastic constants  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ , and  $C_{33}$  linearly increase monotonously when pressure is enhanced. Moreover,  $C_{44}$  decreases very slowly with the elevated pressure.

Base on the obtained elastic constants of  $\beta$ - $\text{Si}_3\text{N}_4$ , we also investigated its polycrystalline elastic properties, such as Voigt bulk modulus ( $B_V$ ), the Reuss bulk modulus ( $B_R$ ), the Voigt shear modulus ( $G_V$ ), and the Reuss shear modulus ( $G_R$ ). By using the Voigt-Reuss-Hill average method [33, 34], the bulk modulus  $B = (B_R + B_V)/2$  and the shear modulus  $G = (G_R + G_V)/2$  are derived, then the Young’s modulus  $E$  is also obtained:  $E = 9BG/(3B + G)$  using the above  $B$  and  $G$ . The calculated results are summarized in Table 3. At  $T = 0$  K and  $P = 0$  GPa, the calculated bulk modulus  $B$  is 257.84 GPa, which is much accords with the experimental data of 259 GPa by using Brillouin scattering [9].

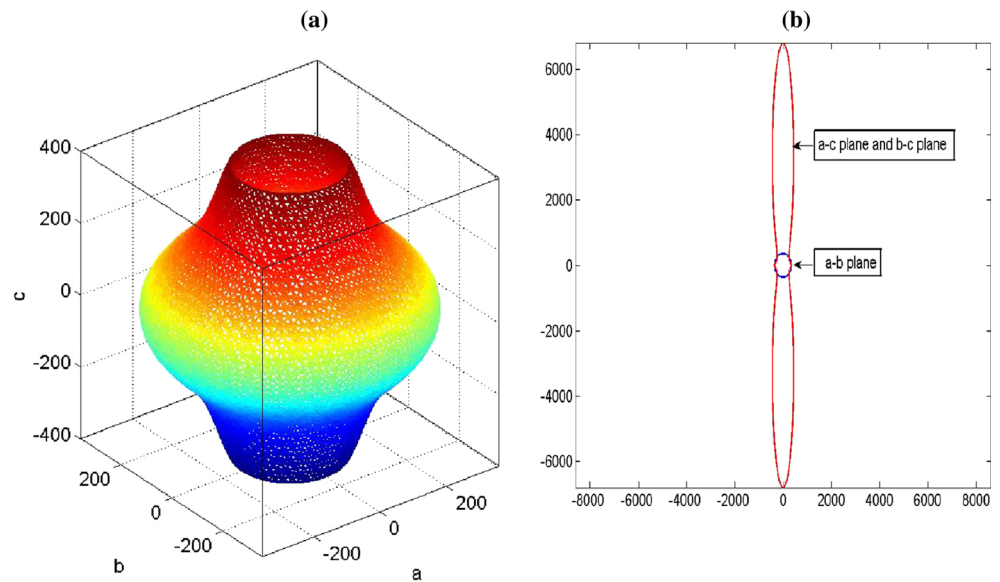


**Fig. 3** The present LDA calculated elastic constants of  $\beta$ - $\text{Si}_3\text{N}_4$  as a function of pressure at zero temperature

**Table 3** The present LDA calculated bulk modulus  $B$  (GPa), shear modulus  $G$  (GPa), Young Modulus  $E$  (GPa), Poisson’s ratio  $\sigma$ , the ratio of the shear modulus  $G$  to the bulk modulus  $B$  ( $B/G$ ), and the compressional wave velocities  $V_l$  (km/s), the shear wave velocities  $V_t$  (km/s), the average wave velocity  $V_m$  (km/s), and Debye temperature  $\Theta$  (K) of the  $\beta$ - $\text{Si}_3\text{N}_4$  under high pressures at 0 K

	B	G	E	$\sigma$	B/G	$V_l$	$V_t$	$V_m$	$\Theta$
0	257.84	135.20	345.25	0.277	1.91	11.49	6.38	7.11	961.41
5	274.89	133.99	345.79	0.290	2.05	11.58	6.29	7.02	957.19
10	292.43	130.09	339.87	0.306	2.25	11.63	6.15	6.87	942.24
15	310.69	128.51	338.82	0.318	2.42	11.73	6.06	6.78	935.30
20	327.82	127.53	338.67	0.328	2.57	11.83	5.99	6.71	930.44
25	343.83	123.48	330.84	0.340	2.78	11.86	5.85	6.56	914.65
30	359.94	126.45	339.58	0.343	2.85	12.01	5.87	6.60	923.76
35	375.91	117.84	320.07	0.358	3.19	11.98	5.63	6.34	891.55

**Fig. 4** **a** The direction dependence of Young's modulus under zero pressure and **b** its projections onto the a-b, b-c, and a-c plane for  $\beta$ -Si<sub>3</sub>N<sub>4</sub> under zero pressure (unit, GPa)



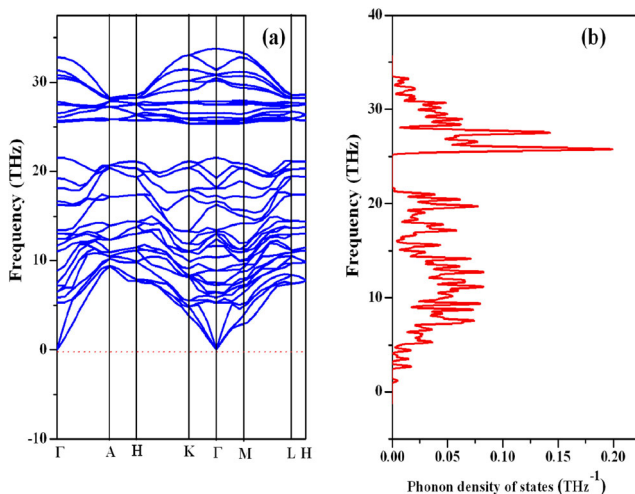
The ratio  $B/G$  has been proposed to evaluate the ductile or brittle character of materials by Pugh [35]. The critical ratio  $B/G$  value is 1.75. If  $B/G > 1.75$ , the material behaves in a ductile manner, otherwise,  $B/G < 1.75$  in a brittle manner. From Table 3, it can be found that the ratio of  $B/G$  is above 1.75 from 1.91 of 0 GPa to 3.19 of 35 GPa, however, the values increase with increasing pressure gradually. Thus, it becomes more and more ductile with increasing applied pressure. The Poisson's ratios of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> are calculated using the formula:  $\sigma = (3B - 2G)/[2(3B + G)]$ , which are listed in Table 3.

Finally, we obtained the compressional wave velocities  $V_l$ , the shear wave velocities  $V_t$ , and the average wave velocity  $V_m$  under 0 GPa up to 35 GPa, according to Navier's equations [36]. Three wave velocities  $V_l$ ,  $V_t$ , and  $V_m$  are listed in Table 3. The Debye temperature ( $\Theta$ ) can be deduced from the above wave velocity and summarized in Table 3. Our calculated  $\Theta$  at  $T=0$  K and

$P=0$  GPa is 964.41 K (see Table 3), which is quite consistent with experimental data  $923 \pm 5$  K [7]. This indicates that our calculated Debye temperature values under high pressure also are trustable.

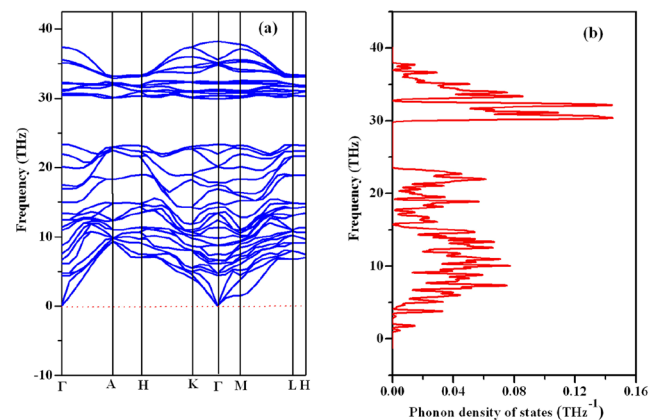
In order to display the elastic anisotropy more visually, we presented the direction-dependent Young's modulus ( $E$ ). The 3D figure of directional dependences of the reciprocal of  $E$  for the  $\beta$ -Si<sub>3</sub>N<sub>4</sub> can be defined by the following equation due to crystal structure [37]. We plotted the  $E$  in Fig. 4a. It is shown clearly that the  $E$  shows a high degree of anisotropy along different crystallographic. From the projections of  $E$  in Fig. 4b, the anisotropy of the a-b plane seems alike, but that of the a-c or b-c planes is serious, which reveals the elastic anisotropy of  $\beta$ -Si<sub>3</sub>N<sub>4</sub>.

### 3.3 Lattice Dynamics

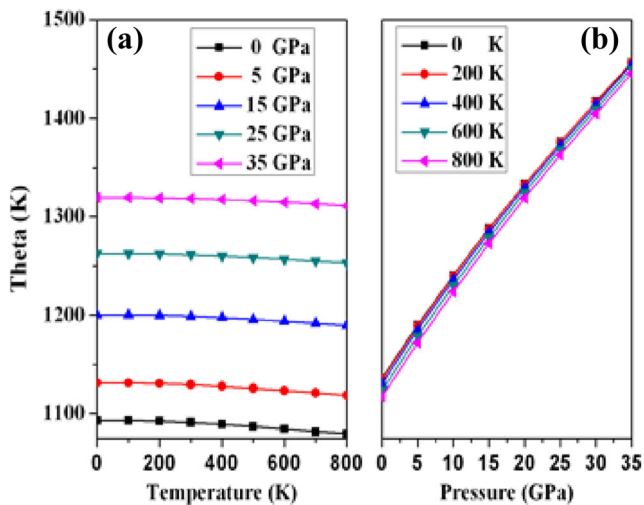


**Fig. 5** Phonon dispersion curves (a) and Phonon density of states (b) for  $\beta$ -Si<sub>3</sub>N<sub>4</sub> at  $T=0$  K and  $P=0$  GPa

Figure 5 plot the phonon dispersion curves along with the total phonon density of states of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> at 0 GPa. It can be seen



**Fig. 6** Phonon dispersion curves (a) and Phonon density of states (b) for  $\beta$ -Si<sub>3</sub>N<sub>4</sub> at  $T=0$  K and  $P=35$  GPa



**Fig. 7** Debye temperature ( $\Theta$ ) versus temperature at various pressures (a) and Debye temperature ( $\Theta$ ) versus pressure at various temperature (b). We have also calculated the heat capacity, entropy, Grüneisen parameter, and thermal expansion coefficient of  $\beta$ - $\text{Si}_3\text{N}_4$  at 300 K under different pressures. The theoretical results are presented in Table 4. No experimental and theoretical data of thermal parameters as a function of pressure and temperature are available in the literature for comparison

that the phonon dispersion curves and total phonon densities of states at 0 GPa agree well with previous calculation [12] and experimental data [38], they show similar profiles. From Figs. 5 and 6, there is a shift of position under pressure at  $P=0$  and 35 GPa. Additionally, a stable crystalline structure requires all phonon frequencies to be positive. Figures 5 and 6 shows the phonon dispersion curves of  $\beta$ - $\text{Si}_3\text{N}_4$  at 0 and 35 GPa. As what is shown in Figs. 5 and 6, no imaginary phonon frequency was found in the whole Brillouin zone direction, indicating the dynamical stabilities of  $\beta$ - $\text{Si}_3\text{N}_4$  up to 35 GPa.

### 3.4 Thermal Properties

By using the quasi-harmonic Debye model, we obtained the thermal properties of  $\beta$ - $\text{Si}_3\text{N}_4$  under 0 GPa up to 35 GPa and 0 K up to 800 K.

**Table 4** The values of heat capacity of constant volume  $C_V$  (J/mol\*K), heat capacity of constant pressure  $C_P$  (J/mol\* K), Entropy  $S$  (J/mol\*K), Grüneisen parameter  $\gamma$ , and thermal expansion coefficient  $\alpha$  ( $10^{-5}/\text{K}$ ) for  $\beta$ - $\text{Si}_3\text{N}_4$  at 300 K under different pressures

$P/\text{GPa}$	$C_V$	$C_P$	$S$	$\gamma$	$\alpha$
0	97.57	98.01	54.34	1.84	0.83
5	94.07	94.45	51.04	1.79	0.74
10	90.87	91.18	48.15	1.75	0.66
15	87.92	88.19	45.61	1.71	0.60
20	85.12	85.40	43.33	1.67	0.54
25	82.60	82.80	41.28	1.64	0.50
30	80.20	80.37	39.43	1.61	0.46
35	77.93	78.09	37.74	1.59	0.42

Debye temperature ( $\Theta$ ) as the function of the pressure and temperature illustrated by our calculated results is plotted in Fig. 7. It can be found that  $\Theta$  is nearly constant at low temperature and decreases linearly with increasing temperature as shown in Fig. 7a. When the temperature is constant, the  $\Theta$  increases almost linearly with applied pressure as shown in Fig. 7b. In the quasi-harmonic Debye model used here, the  $\Theta$  of  $\beta$ - $\text{Si}_3\text{N}_4$  turns out to be 1093.18 K at the  $T=0$  and  $P=0$ , which is a bit larger the value 923  $\pm$  5 K [7].

## 4 Conclusions

In summary, we have presented a theoretical study the structural, elastic and thermal properties  $\beta$ - $\text{Si}_3\text{N}_4$  using GGA-PBE and quasi-harmonic Debye model. Our theoretical results of lattice constants  $a$  and  $c$  are found to be in good agreement with experimental data. Through calculations, the elastic constants, bulk modulus, shear modulus, Young Modulus, Poisson's ratio, the ratio of the shear modulus to the bulk modulus, the wave velocities, and Debye temperature under high pressure and the mechanical anisotropies of  $\beta$ - $\text{Si}_3\text{N}_4$  are also calculated for the first time. By the elastic stability criteria and phonon calculation, it is predicted that  $\beta$ - $\text{Si}_3\text{N}_4$  is stable up to 35 GPa. Moreover, we predict the thermal properties with pressure and temperature.

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