

First-principles calculations of electronic properties of $P\bar{6}$ - Si_3N_4 and $P\bar{6}'$ - Si_3N_4 under pressure

Xiaoqian Wang^{1, a}, Hui Lv^{1, b}, Yanhua Yin^{1, c} and Mei Sun^{1, d}

¹School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing 100081, China.

^awxq_anne@163.com, ^b1064536522@qq.com, ^cyinyh@bit.edu.cn, ^d993277402@qq.com

Keywords: First-principles, Electronic property, High pressure

Abstract. Using first-principles computations, the structural, electronic properties of $P\bar{6}$ - and $P\bar{6}'$ - Si_3N_4 in the pressure ranges of 40-50 GPa were investigated systematically, and the band structures and density of states have been analyzed in detail. the results show both $P\bar{6}$ - and $P\bar{6}'$ - Si_3N_4 are insulators, and there have no structural phase transformation under the pressure 40-50GPa.

1. Introduction

Silicon nitride (Si_3N_4) has received great attentions as a high-performance engineering ceramic because of its mechanical strength and hardness in combination with high thermal stability and good resistance to corrosion and wear^[1-3]. In particular, due to its superior mechanical properties, Si_3N_4 has been used as engine components, extrusion dies, cutting tools, and other industrial applications^[4].

As we all know, there are two polymorphic forms of Si_3N_4 with very similar structures, namely α (P31c) and β (P63/m) phases. Both configurations are hexagonal crystal structures with the only difference in stacking sequences of the layered atoms perpendicular to the c axis^[5]. Additionally, β - Si_3N_4 is very stable and can be obtained from a transformation of α to β phase at high temperatures. Andreas Zerr et al^[6]. firstly synthesize a third polymorph of silicon nitride under high pressure above 15 GPa and at temperature exceeding 2000K, which has a cubic spinel structure (γ - Si_3N_4 , $Fd\bar{3}m$). And the hardness of γ - Si_3N_4 is significantly greater than these two hexagonal polymorphs. Soon after, Andreas Zerr discovered a new phase (δ - Si_3N_4 , P3)^[7]. By some mechanism reasons, Kroll P observed the $\beta \rightarrow$ willemite-II (wII phase, $I\bar{4}3d$) transformation^[8]. Recently, Si_3N_4 was found to transform to "post-spinel" phase instead of spinel under high pressure^[8-10]. In 2011, Xu et al.^[11] found other new polymorphs for Si_3N_4 , namely the $P\bar{6}$ and $P\bar{6}'$ phases.

During the past decade, a various properties of Si_3N_4 have been theoretically and experimentally studied based on density functional theory, such as structural and electronic properties^[1,12,13], vibrational property^[13,14] and thermal property^[15]. In the above studies, a common problem is that the influence of temperature and/or pressure on the properties were not taken into account. In addition, more attention have focused on the β - Si_3N_4 and γ - Si_3N_4 , but the properties of $P\bar{6}$ - and $P\bar{6}'$ - Si_3N_4 have been scarcely studied. Thus, in this work, we carry out a detailed investigation of $P\bar{6}$ - and $P\bar{6}'$ - Si_3N_4 under pressure 40-50 GPa through the first-principles calculations.

2. Computational details and models

The calculations are performed using the ab initio pseudopotential density functional method implemented in the CASTEP code^[16]. Exchange-correlation terms are treated by Perdew-Burke-Ernzerh (PBE) in generalized gradient approximation (GGA)^[17]. Local density approximation (LDA) is a useful tool to study ground state physical properties, but LDA ignores the impact of the non-uniformity of electron density, using LDA may overestimate bond energy in

some situation. Previous theoretical work showed that using GGA is more accurate than LDA for covalent bond system^[18]. Ultrasoft pseudopotentials are expanded within a plane-wave basis set with a 500 eV cut off energy in the processes of optimization of the $P\bar{6}$ and $P\bar{6}'$ structures. According to the Monkhorst–Pack method^[19], the k-point sampling in the Brillouin zone (BZ) is set at $4 \times 4 \times 12$. Structural optimization is not performed until the energy change per atom is less than 1×10^{-6} eV, while the forces on the atoms are less than 0.03 eV/Å, and all the stress components are less than 0.05 GPa using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization method^[20]. The optimized crystal structures at 40 GPa are presented in Fig. 1 and their optimized lattice constants at 0 GPa are tabulated in Table 1.

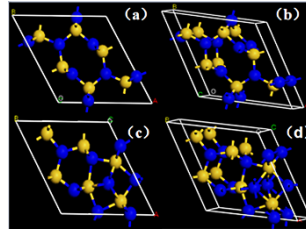


Fig.1 Optimized crystal structures of $P\bar{6}$ - Si_3N_4 and $P\bar{6}'$ - Si_3N_4 at 40 GPa. (a),(b) $P\bar{6}$ - Si_3N_4 , (c),(d) $P\bar{6}'$ - Si_3N_4 . The blue spheres are N atoms, and the yellow ones are Si atoms.

Table 1. Lattice constants, volume of (a) $P\bar{6}$ - Si_3N_4 and (b) $P\bar{6}'$ - Si_3N_4 (at 0 GPa) compared with other results.

	a/nm	c/nm	V/ $10^{-3}m^3$
a (Cal.)	0.7633	0.2915	147.08
a(Ref.[21])	0.7632	0.2915	147.22
b(Cal.)	0.7369	0.2809	132.10
b(Ref.[21])	0.7369	0.2810	132.10

3. Results and Discussion

3.1 Equilibrium crystal structures

The Si_3N_4 polymorphs are optimized at 0 GPa and the calculated lattice constants of the $P\bar{6}$ and $P\bar{6}'$ phases are listed in Table 1. As shown in Table 1, our calculations are well consistent with the theoretical results for $P\bar{6}$ -, $P\bar{6}'$ - Si_3N_4 . Compared with the theoretical data^[21], the maximum relative error of the computed equilibrium lattice constants for $P\bar{6}$ -, $P\bar{6}'$ - Si_3N_4 is only 0.08% and 0.04%, respectively, which is within the general accuracy of first-principles method using GGA (usually less than 2%), implying that our calculations are valid and reliable.

3.2 Electronic properties under pressure

Fig.2 shows the band structures calculated along high-symmetry of $P\bar{6}$ - and $P\bar{6}'$ - Si_3N_4 at 40 GPa, and the Fermi energy is set as 0 eV. We remark fundamental band gaps for the two phases, and the magnitudes are found to be about 4.719 eV for $P\bar{6}$ - Si_3N_4 and 3.167 eV for $P\bar{6}'$ - Si_3N_4 which are underestimated by GGA so that $P\bar{6}$ - Si_3N_4 and $P\bar{6}'$ - Si_3N_4 are both probably insulators.

To obtain a deeper insight into the electronic property and to elucidate the major contribution of orbits in the band structure, we have also calculated total and partial density of states (TDOS and PDOS) at 40 GPa for $P\bar{6}$ - Si_3N_4 and $P\bar{6}'$ - Si_3N_4 near the Fermi level and the results are displayed in Figs.3 and 4. The density of states (DOS) also can provide important information of physical properties of materials^[22]. As shown in Figs. 3 and 4, it is evident that these two phases are alike, indicating the similarity in chemical bonding. Energy states are scarcely crossing the Fermi level, which signifies that $P\bar{6}$ - Si_3N_4 and $P\bar{6}'$ - Si_3N_4 would both demonstrate insulative property. At lower energy level, the valence band is divided into two sub-band groups. Moreover, there is an energy gap between these two sub-band groups from -14.0 to -10.5 eV for $P\bar{6}$ - Si_3N_4 and -13.5 to -11.2 eV for $P\bar{6}'$ - Si_3N_4 . The main bonding peaks locate in the energy range between the Fermi level and -10

eV, in which the most dominant contribution comes from the p states of the N atoms and a smaller amount of s, p orbitals of Si atoms. While the peaks locating between -14 and -20 eV also originate from N p states, with a smaller contribution of Si s and Si p states. Additionally, the DOS profiles of both $\text{P}\bar{6}$ - and $\text{P}\bar{6}'$ - Si_3N_4 at higher energy level indicate that Si 3s and N 2p states have almost the same contribution to the conduction band and are seriously overlapping, showing Si 3s and N 2p states are strongly hybridized, and conduction band is mainly composed by p bands of Si atoms.

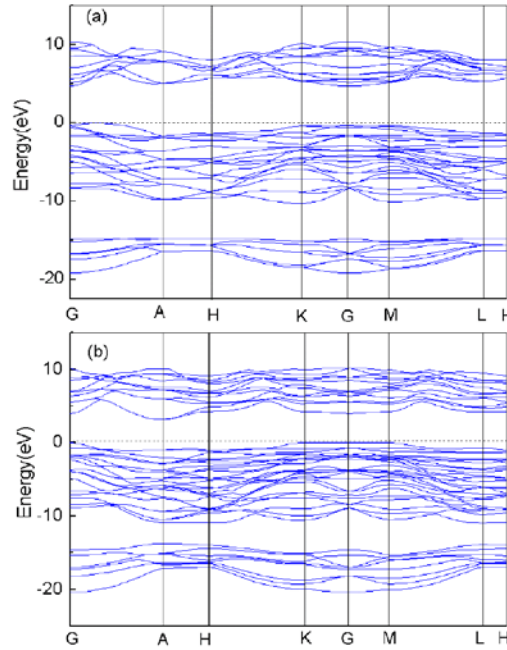


Fig.2 Band structures calculated along high-symmetry of (a) $\text{P}\bar{6}$ - Si_3N_4 and (b) $\text{P}\bar{6}'$ - Si_3N_4 at 40 GPa

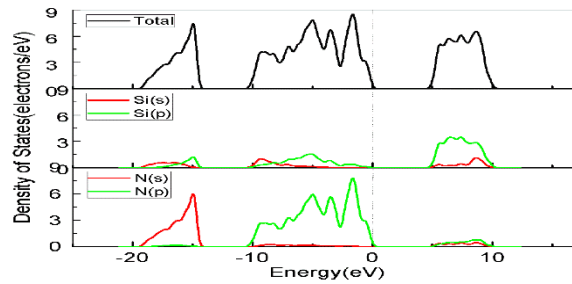


Fig. 3 Density of states (TDOS and PDOS) of $\text{P}\bar{6}$ - Si_3N_4 at 40 GPa.

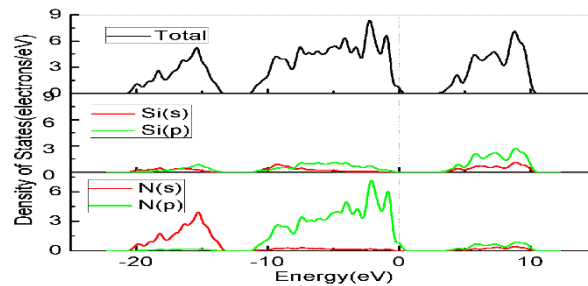


Fig. 4 Density of states (TDOS and PDOS) of $\text{P}\bar{6}'$ - Si_3N_4 at 40 GPa.

To understand the variation of the DOS of $\text{P}\bar{6}$ - Si_3N_4 and $\text{P}\bar{6}'$ - Si_3N_4 with applied pressure, the total density of states (TDOS) at 40 and 50 GPa near the Fermi level are also investigated, as

displayed in Figs. 5 and 6. By comparison of DOS of $P\bar{6}$ - Si_3N_4 and $P\bar{6}'$ - Si_3N_4 at 40 and 50 GPa, it is interesting to observe that the shapes of the peaks present slight change. These results suggest that $P\bar{6}$ - Si_3N_4 and $P\bar{6}'$ - Si_3N_4 both remain structural stable and have no structural phase transformation under the pressure 40-50 GPa. It can be found that there exhibits a slight offset of TDOS of $P\bar{6}$ - Si_3N_4 and $P\bar{6}'$ - Si_3N_4 with increasing the external pressure. This could be attributed to that the change of potential interactions has occurred because of the smaller atomic distance under compression, which results in the shifting of the overall electron energy levels to the low value region. Thus, the decrease of TDOS with the increment of pressure can be observed.

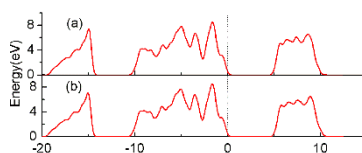


Fig.5 The density of states (TDOS) of $P\bar{6}$ - Si_3N_4 under different pressure (a) 40GPa and (b) 50 GPa.

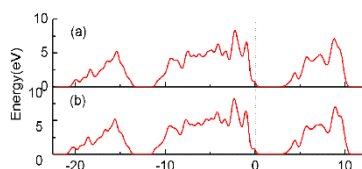


Fig.6 The density of states (TDOS) of $P\bar{6}'$ - Si_3N_4 under different pressure (a) 40GPa and (b) 50 GPa.

4. Conclusions

In this paper, the electronic properties of $P\bar{6}$ - and $P\bar{6}'$ - Si_3N_4 under pressure have been investigated using first-principles method. The computed lattice constants and volumes of both $P\bar{6}$ - and $P\bar{6}'$ - Si_3N_4 are consistent with the published theoretical data, implying the effectiveness and accuracy of the proposed theoretical models. According to the calculated energy band structures and density of states, these two structures turn out to be insulators. and these two structures both remain structural stable and have no structural phase transformation under the pressure 40-50GPa.

Reference

- [1] A.Y. Liu, M.L. Cohen, Structure properties and compressibility materials: β - Si_3N_4 hypothetical C_3N_4 , Phys Rev B. 41(1990)10727-10734.
- [2] Y.H. Duan, K.M. Zhang, Electronic Structural Properties of β - C_3N_4 , β - Si_3N_4 and β - Ge_3N_4 , Phys Stat Sol B. 200(1997)499-508.
- [3] S.D. Mo, L. Ouyang, W.Y. Ching, Interesting physical properties of the new spinel phase of Si_3N_4 and C_3N_4 , Phys Rev Lett. 83(1999)5046-5049.
- [4] S. Ogata, N. Hirotsaki, C. Kocer, H. Kitagawa, An ab initio calculation of the ideal tensile strength of β -silicon nitride, Phys Rev B. 64(2001) 607-611.
- [5] W.Y. Ching, L. Ouyang, G.D. Gale, Full ab initio geometry optimization of all known crystalline phases of Si_3N_4 , Phys Rev B. 61(2000)8696-8700.
- [6] A. Zerr, G. Miehe, G. Serghiou, Synthesis of cubic silicon nitride, Nature. 400(1999) 340-342.

- [7] A. Zerr, A new high-pressure δ -Phase of Si_3N_4 , *Phys Stat Sol B*. 227(2001)R4-R6.
- [8] P. Kroll, J. Solid, Pathways to metastable nitride structures, *State Chem*. 176(2003) 530-537.
- [9] P. Kroll, J. von Appen, Post-spinel phases of silicon nitride, *Phys Stat Sol B*. 226(2001)R6-R7.
- [10] T.Yamanaka, A.Uchida, Y. Nakamoto, Structural transition of post-spinel phases CaMn_2O_4 , CaFe_2O_4 , and CaTi_2O_4 under high pressures up to 80 GPa, *Am Mineral*. 226(2001)R6-R7.
- [11] B. Xu, J. Dong, P. F. McMillan, Equilibrium and metastable phase transitions in silicon nitride at high pressure: A first-principles and experimental study, *Phys Rev B*. 84(2011)014113.
- [12] M. Yashima, Y. Ando, Tabira, Crystal structure and electron density of α -silicon nitride: Experimental and theoretical evidence for the covalent bonding and charge transfer, *J Phys Chem B*. 111(2007)3609-3613.
- [13] L. Giacomazzi, P. Umari, First-principles investigation of electronic, structural, and vibrational properties of α - Si_3N_4 , *Phys Rev B*. 80(2009)144201.
- [14] Y. Cai, L.Zhang, Q. Zeng, First-principles study of vibrational and dielectric properties of β - Si_3N_4 , *Phys Rev B*. 74(2006)3840-3845.
- [15] C.M. Fang, G.A.D. Wijs, H.T.Hintzen, Phonon spectrum and thermal properties of cubic Si_3N_4 from first-principles calculations, *J Appl Phys*. 93(2003)5175-5180.
- [16] M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients, *Rev Mod Phys*. 64(1992)1045-1097.
- [17] J.P. Perdew, K. Burke, M. Ernzerhof, Erratum: Generalized Gradient Approximation Made Simple, *Phys Rev Lett*. 77(1996) 3865-3868.
- [18] M. Schwarz, G. Miehe, A. Zerr, Spinel- Si_3N_4 : Multi-Anvil Press Synthesis and Structural Refinement, *Adv Mater*. 12(2000)883-887.
- [19] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, *Phys Rev B*. 13(1976)5188-5192.
- [20] T.H. Fischer, J. Almlof, General methods for geometry and wave function optimization, *J Phys Chem*. 96(1992)9768-9774.
- [21] B. H.Yu, D. Chen, Phase transition character and thermodynamic modeling of the and hexagonal Si-N system supplemented by first-principles calculations, *J Alloys Comp*. 581(2013)747-752.
- [22] P. Wang, Y. Cheng, X.H. Zhu, First principles investigations on elastic and electronic properties of BaHfN_2 under pressure, *J Alloys Comp*. 526(2012)74.