First-principles calculations of electronic properties of \(P\bar{6} - \text{Si}_3\text{N}_4\) and \(P\bar{6}' - \text{Si}_3\text{N}_4\) under pressure

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**Abstract.** Using first-principles computations, the structural, electronic properties of \(P\bar{6} - \text{Si}_3\text{N}_4\) and \(P\bar{6}' - \text{Si}_3\text{N}_4\) 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 \(P\bar{6} - \text{Si}_3\text{N}_4\) and \(P\bar{6}' - \text{Si}_3\text{N}_4\) are insulators, and there have no structural phase transformation under the pressure 40-50 GPa.

1. Introduction

Silicon nitride (Si\(_3\)N\(_4\)) 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\(_3\)N\(_4\) 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\(_3\)N\(_4\) with very similar structures, namely \(\alpha\) (P31c) and \(\beta\) (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, \(\beta\)-Si\(_3\)N\(_4\) is very stable and can be obtained from a transformation of \(\alpha\) to \(\beta\) 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 (\(\gamma\)-Si\(_3\)N\(_4\), Fd\(_3\)m). And the hardness of \(\gamma\)-Si\(_3\)N\(_4\) is significantly greater than these two hexagonal polymorphs. Soon after, Andreas Zerr discovered a new phase (\(\delta\)-Si\(_3\)N\(_4\), P3)\([7]\). By some mechanism reasons, Kroll P observed the \(\beta\rightarrow\) willemite-II (wII phase, I\(_4\)3d) transformation\([8]\). Recently, Si\(_3\)N\(_4\) 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\(_3\)N\(_4\), namely the \(P\bar{6}\) and \(P\bar{6}'\) phases.

During the past decade, various properties of Si\(_3\)N\(_4\) 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 \(\beta\)-Si\(_3\)N\(_4\) and \(\gamma\)-Si\(_3\)N\(_4\), but the properties of \(P\bar{6} - \text{Si}_3\text{N}_4\) and \(P\bar{6}' - \text{Si}_3\text{N}_4\) have been scarcely studied. Thus, in this work, we carry out a detailed investigation of \(P\bar{6} - \text{Si}_3\text{N}_4\) and \(P\bar{6}' - \text{Si}_3\text{N}_4\) 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 $1 \times 10^{-6}$ 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$_3$N$_4$ and $P\bar{6}'$-Si$_3$N$_4$ at 40 GPa. (a),(b) $P\bar{6}$-Si$_3$N$_4$, (c),(d) $P\bar{6}'$-Si$_3$N$_4$. The blue spheres are N atoms, and the yellow ones are Si atoms.](image)

Table 1. Lattice constants, volume of (a) $P\bar{6}$-Si$_3$N$_4$ and (b) $P\bar{6}'$-Si$_3$N$_4$ (at 0 GPa) compared with other results.

<table>
<thead>
<tr>
<th></th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>V/10$^{-3}$ m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Cal.)</td>
<td>0.7633</td>
<td>0.2915</td>
<td>147.08</td>
</tr>
<tr>
<td>a(Ref.[21])</td>
<td>0.7632</td>
<td>0.2915</td>
<td>147.22</td>
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<tr>
<td>b(Cal.)</td>
<td>0.7369</td>
<td>0.2809</td>
<td>132.10</td>
</tr>
<tr>
<td>b(Ref.[21])</td>
<td>0.7369</td>
<td>0.2810</td>
<td>132.10</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1 Equilibrium crystal structures

The Si$_3$N$_4$ 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$_3$N$_4$. Compared with the theoretical data \[^{[21]}\], the maximum relative error of the computed equilibrium lattice constants for $P\bar{6}$-, $P\bar{6}'$-Si$_3$N$_4$ 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$_3$N$_4$ 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$_3$N$_4$ and 3.167 eV for $P\bar{6}'$-Si$_3$N$_4$ which are underestimated by GGA so that $P\bar{6}$-Si$_3$N$_4$ and $P\bar{6}'$-Si$_3$N$_4$ 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$_3$N$_4$ and $P\bar{6}'$-Si$_3$N$_4$ 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$_3$N$_4$ and $P\bar{6}'$-Si$_3$N$_4$ 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$_3$N$_4$ and -13.5 to -11.2 eV for $P\bar{6}'$-Si$_3$N$_4$. 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 $P\bar{6}$- and $P\bar{6}'$-$Si_3N_4$ at higher energy level indicate that Si 3s and N 2p states have almost the same contribution to the conduction band and are serious overlapping, showing Si 3s and N 2p states are strongly hybridized, and conduction band is mainly composed by p bands of Si atoms.

![Band structures calculated along high-symmetry of (a) $P\bar{6}$-$Si_3N_4$ and (b) $P\bar{6}'$-$Si_3N_4$ at 40 GPa](image)

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

![Density of states (TDOS and PDOS) of $P\bar{6}$-$Si_3N_4$ at 40 GPa.](image)

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

![Density of states (TDOS and PDOS) of $P\bar{6}'$-$Si_3N_4$ at 40 GPa.](image)

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

To understand the variation of the DOS of $P\bar{6}$-$Si_3N_4$ and $P\bar{6}'$-$Si_3N_4$ 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$_3$N$_4$ and $P\bar{6}'$-Si$_3$N$_4$ 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$_3$N$_4$ and $P\bar{6}'$-Si$_3$N$_4$ 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$_3$N$_4$ and $P\bar{6}'$-Si$_3$N$_4$ 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$_3$N$_4$ under different pressure (a) 40GPa and (b) 50 GPa.

Fig. 6 The density of states (TDOS) of $P\bar{6}'$-Si$_3$N$_4$ 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$_3$N$_4$ 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$_3$N$_4$ 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