Mechanical, Anisotropic, and Electronic Properties of XN (X = C, Si, Ge): Theoretical Investigations

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Received: 12 June 2017; Accepted: 3 August 2017; Published: 8 August 2017

Abstract: The structural, mechanical, elastic anisotropic, and electronic properties of Pbca-XN (X = C, Si, Ge) are investigated in this work using the Perdew–Burke–Ernzerhof (PBE) functional, Perdew–Burke–Ernzerhof for solids (PBEsol) functional, and Ceperly and Alder, parameterized by Perdew and Zunger (CA–PZ) functional in the framework of density functional theory. The achieved results for the lattice parameters and band gap of Pbca-CN with the PBE functional in this research are in good accordance with other theoretical results. The band structures of Pbca-XN (X = C, Si, Ge) show that Pbca-SiN and Pbca-GeN are both direct band gap semiconductor materials with a band gap of 3.39 eV and 2.22 eV, respectively. Pbca-XN (X = C, Si, Ge) exhibits varying degrees of mechanical anisotropic properties with respect to the Poisson’s ratio, bulk modulus, shear modulus, Young’s modulus, and universal anisotropic index. The (001) plane and (010) plane of Pbca-CN/SiN/GeN both exhibit greater elastic anisotropy in the bulk modulus and Young’s modulus than the (100) plane.

Keywords: C/Si/Ge-group-V compounds; electronic properties; mechanical properties; anisotropic properties

1. Introduction

In the last few decades, nitride-based ceramics such as silicon nitride (Si3N4) have attracted increasing attention from researchers in the ceramics, mechanical, and aerospace industries, as well as in fields such as solar cells, as they have a wide range of applications [1–8]. This is due to their significant chemical stability, good compression resistance, corrosion resistance, high hardness, good mechanical properties, and good optical performance characteristics. Other stoichiometries like Si3N4, SiN2, and Si2N2(NH) have also been proposed to exist [9–14]. Silicon and germanium-based compounds and alloys such as the Si/Ge-group-III and Si/Ge-group-V compounds have been widely investigated [15–17].

CxnNy with different stoichiometries is often used as a potential superhard material [18–21]. Li et al. [18] have reported a novel body-centered tetragonal CN2 named bct-CN2, using the newly-developed particle swarm optimization algorithm for crystal structure prediction. They found that the hardness of bct-CN2 is 77.4 GPa, and it is an indirect wide gap semiconductor material with a band gap of 3.6 eV. Wang et al. [19] suggested a new carbon nitride phase consisting of sp3 hybridized bonds, with cubic symmetry and a P213 space group (i.e., c2-CN). Unlike most of the other superhard materials that are insulators or semiconductors, it is a metallic compound, and its Vickers hardness is 82.56 GPa. They found that c2-CN is the most favorable stable crystal structure, with carbon nitride with 1:1 stoichiometry. Using the particle swarm optimization technique, Wei et al. [20] proposed a cubic superhard phase of C3N (c-C3N) with a Vickers hardness of 65 GPa, which is more energetically favorable than the recently proposed o-C3N [21]. o-C3N was proposed by Hao et al. [21]. It has a C2221 phase, and its Vickers hardness is 76 GPa.
CN₂, SiN₂, and GeN₂ were proposed by Manyali et al. [22] using first-principles calculations; they found that SiN₂ and GeN₂ both have mechanical stability, SiN₂ and GeN₂ are characterized by an indirect band gap, and the optical spectra of GeN₂ is within the solar spectrum for CN₂ and SiN₂. The structural, elastic, electronic, and optical properties of Si₃N₂ [23] have been calculated using density functional theory. First, Si₃N₂ has both mechanical and dynamical stability at ambient pressure, and it is still stable at 10–20 GPa. The first-principles plane-wave pseudo-potential (PW-PP) method was applied to investigate the mechanical properties, thermal properties, and phase transition characters of Ge₃N₄ by Luo et al. [24]. The β→wII→γ phase transitions of Ge₃N₄ were also successfully predicted by them; at 300 K, the calculated P₁ of the β→wII transition is 10.7 GPa, and the calculated P₁ of the β→γ transition is 14.26 GPa at 1200 K. The bulk moduli of β-Ge₃N₄, wII-Ge₃N₄, and γ-Ge₃N₄ are 179 GPa, 187 GPa, and 220 GPa, respectively. Pseudocubic-Si₃P₄ and Ge₃P₄ [25] were proposed by first-principles calculations for investigating the electronic, mechanical, and optical properties of pseudocubic-Si₃P₄ and Ge₃P₄. The bulk modulus and shear modulus of pseudocubic-Si₃P₄ and Ge₃P₄ are 76 GPa and 58 GPa, and 60 GPa and 47 GPa, respectively. In addition, pseudocubic-Si₃P₄ and Ge₃P₄ are both indirect and narrow band gap semiconductor materials, with band gaps of 0.24 eV and 0.15 eV, respectively.

Recently, Wei et al. [26] investigated the stability and electronic and mechanical properties of Pbca-CN using first-principles calculations. The electronic properties and elastic anisotropy in bulk modulus, shear modulus, and Poisson’s ratio of Pbca-CN are not fully represented. We proposed Pbca-SiN and Pbca-GeN (space group: Pbca), which have a structure based on Pbca-CN, with silicon atoms or germanium atoms substituting carbon atoms. In this work, the stability as well as structural, mechanical, electronic, and elastic anisotropy properties of Pbca-XN (X = C, Si, Ge) were systematically investigated.

2. Materials and Methods

The theoretical calculations were carried out using first-principles density functional theory (DFT) [27,28]. The calculations were performed using the Cambridge Serial Total Energy Package (CASTEP) code [29]. The generalized gradient approximation (GGA) parameterized by Perdew–Burke–Ernzerhof (PBE) [30] functional, Perdew–Burke–Ernzerhof for solids (PBEsol) [31] functional, and the local density approximation (LDA) parameterized by Ceperly and Alder, parameterized by Perdew and Zunger (CA-PZ) [32,33] exchange-correlation functional were employed for the self-consistent total energy calculations and geometry optimization. The C/Si/Ge: 2s²2p²/3s²3p²/4s²4p² and N: 2s²2p³ electrons were explicitly treated as valence electrons. The energy cutoff for the plane wave basis set was chosen to be 520/500/440 eV for CN/SiN/GeN in the Pbca phase. The conjugate gradient method was used for the relaxation of structural parameters. The k-point samplings with 2π × 0.025 Å⁻¹ (7 × 9 × 10/5 × 7 × 8/5 × 7 × 8) in the Brillouin zone were performed using the Monkhorst–Pack scheme [34] for CN/SiN/GeN in Pbca phase. The structural parameters optimizations were determined using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [35], with the flowing thresholds for converged structures: energy change less than 5 × 10⁻⁶ eV per atom, residual force below 0.01 eV/Å, stress less than 0.02 GPa, and displacement of atoms during the geometry optimization less than 0.0005 Å. The phonon frequencies were calculated using linear response theory [36]. The electronic band structures of the CN/SiN/GeN in Pbca phase were calculated utilizing the Heyd–Scuseria–Ernzerhof (HSE06) [37,38] hybrid functional.

3. Discussion

3.1. Structural Properties

In the newly-formed (Pbca phase) solid, all the nitrogen atoms have sp² hybridizations and all the carbon/silicon/germanium atoms have sp³ hybridization with their nearest neighboring N and C/Si/Ge atoms. The crystal structures of CN/SiN/GeN in Pbca phase are shown in Figure 1a.
3. Discussion

3.1. Structural Properties

In the newly-formed (Pbca phase) solid, all the nitrogen atoms have sp hybridization with their nearest neighboring N and Si/Ge atoms. The crystal structures of CN/SiN/GeN in the Pbca phase along the (001) direction and (010) direction are shown in Figure 1b,c, respectively. The eight-membered rings are normal to the (001) direction in the structure of Pbca-CN/SiN/GeN, and the six-membered rings are normal to the (010) direction. The optimal lattice parameters of Pbca-CN/SiN/GeN, together with the previous results [27,39] of Pbca-CN are listed in Table 1. The optimized lattice parameters are \(a = 5.504 \text{ Å}, b = 4.395 \text{ Å},\) and \(c = 4.041 \text{ Å},\) which are in excellent agreement with [27,39]. In addition, taking into account the van der Waals forces, we also calculated the lattice parameters of Pbca-CN/SiN/GeN and diamond, c-BN using the dispersion-corrected Perdew–Burke–Ernzerhof (PBE + D) [40]. For diamond and c-BN, the theoretical results obtained by the GGA-PBE level (diamond: 3.566 Å for PBE level, 3.526 Å for CA-PZ [41], experimental value 3.567 Å [42]; c-BN: 3.626 Å for PBE level, 3.569 Å for CA-PZ [43], experimental value 3.620 Å [44]) are closer to the experimental values; the obtained results of c-BN and diamond using PBE + D are not much different from those obtained by PBE functional compared to corresponding experimental values, so the results obtained by the GGA-PBE level are all used in our paper. The lattice parameters of Pbca-XN with X changing from C to Ge are illustrated in Figure 2a. It is clear that the lattice parameters of Pbca-XN increase with X changing from C to Ge. From CN to SiN, the lattice parameters increase 31.4\%, 21.52\%, and 20.7\% for \(a, b,\) and \(c\) of SiN compared to CN, while the lattice parameters increase 8.25\%, 5.69\%, and 5.84\% for \(a, b,\) and \(c\) of GeN compared to SiN, respectively. This is because the average bond length of Si–N (1.751 Å) is much greater than that of the C–N bond (1.452 Å), and the average bond length of Ge–N (1.871 Å) is slightly longer than that of the Si–N bond.

The C/Si/Ge atoms and N atoms consist of zigzag six-membered rings and eight-membered rings. The C/Si/Ge and N atoms are located at Wyckoff 8c (0.1396, 0.0722, 0.0205)/(0.1507, 0.0794, 0.0291)/(0.1476, 0.0769, 0.0310) and 8c (0.8154, 0.8661, 0.6318)/(0.8038, 0.8690, 0.6241)/(0.8093, 0.8725, 0.6197) sites in Pbca-CN/SiN/GeN, respectively. The crystal structures of CN/SiN/GeN in the Pbca phase along the (001) direction and (010) direction are shown in Figure 1b,c, respectively. The eight-membered rings are normal to the (001) direction in the structure of Pbca-CN/SiN/GeN, and the six-membered rings are normal to the (010) direction. The optimal lattice parameters of Pbca-CN/SiN/GeN, together with the previous results [27,39] of Pbca-CN are listed in Table 1. The optimized lattice parameters are \(a = 5.504 \text{ Å}, b = 4.395 \text{ Å},\) and \(c = 4.041 \text{ Å},\) which are in excellent agreement with [27,39]. In addition, taking into account the van der Waals forces, we also calculated the lattice parameters of Pbca-CN/SiN/GeN and diamond, c-BN using the dispersion-corrected Perdew–Burke–Ernzerhof (PBE + D) [40]. For diamond and c-BN, the theoretical results obtained by the GGA-PBE level (diamond: 3.566 Å for PBE level, 3.526 Å for CA-PZ [41], experimental value 3.567 Å [42]; c-BN: 3.626 Å for PBE level, 3.569 Å for CA-PZ [43], experimental value 3.620 Å [44]) are closer to the experimental values; the obtained results of c-BN and diamond using PBE + D are not much different from those obtained by PBE functional compared to corresponding experimental values, so the results obtained by the GGA-PBE level are all used in our paper. The lattice parameters of Pbca-XN with X changing from C to Ge are illustrated in Figure 2a. It is clear that the lattice parameters of Pbca-XN increase with X changing from C to Ge. From CN to SiN, the lattice parameters increase 31.4\%, 21.52\%, and 20.7\% for \(a, b,\) and \(c\) of SiN compared to CN, while the lattice parameters increase 8.25\%, 5.69\%, and 5.84\% for \(a, b,\) and \(c\) of GeN compared to SiN, respectively. This is because the average bond length of Si–N (1.751 Å) is much greater than that of the C–N bond (1.452 Å), and the average bond length of Ge–N (1.871 Å) is slightly longer than that of the Si–N bond.

![Figure 1](image-url)

**Figure 1.** The crystal structures of (a) CN/SiN/GeN in the Pbca phase; and CN/SiN/GeN in the Pbca phase along the (b) (001) direction and (c) (010) direction. The blue and red spheres represent the N atoms and C/Si/Ge atoms.
with the previous report [26]. For an orthorhombic phase, the criteria of mechanical stability are [45]:

\[
\begin{align*}
\text{for } & i = 1-6, \ C_{11} - C_{22} + 2C_{12}C_{33} - 2C_{11}C_{33} + C_{12} &> 0; \\
\text{for } & i = 1-6, \ C_{11}C_{22} - C_{22}C_{33} - C_{11}C_{33} + 2C_{12}C_{33} &> 0
\end{align*}
\]

The SiN/GeN in the Pbca phase show mechanical stability under ambient pressure. The phonon dispersion curves can show dynamic stability; the phonon dispersion curves of SiN/GeN in the Pbca phase are illustrated in Figure 3. There is no imaginary frequency in the Brillouin zone, which means SiN/GeN in the Pbca phase can be dynamically stable under ambient pressure. The elastic moduli of Pbca-XN with X changing from C to Ge are illustrated in Figure 2b. It is clear that the elastic moduli of Pbca-XN decrease with X changing from C to Ge. The elastic constants and elastic moduli of other Si_N_x compounds [22,46,47] are also listed in Table 2. The bulk modulus B of Pbca-SiN is slightly smaller than that of SiN_2, o-Si_3N_4, and t-Si_3N_4, while it is slightly larger than Si_3N_2 and t-Si_3N_4. The shear modulus G and Young’s modulus E of Pbca-SiN are similar to the bulk modulus of Pbca-SiN. For Pbca-GeN, its bulk modulus is as large as that of GeN_2. However, its shear modulus and Young’s modulus are slightly smaller than that of GeN_2.

Brittleness and ductility of materials are important properties in crystal physics and engineering sciences. Pugh [48] proposed the ratio of bulk to shear modulus (B/G) as an indication of ductile versus brittle characters. If B/G > 1.75, the material is characterized by a ductile manner; otherwise,

### Table 1. The lattice parameters (in Å) of Pbca-CN/SiN/GeN using different functionals.

| Materials | PBE | PBEsol | CA-PZ | PBE + D |
|-----------|-----|--------|-------|---------|
|           | a   | b     | c     | a       | b     | c |
| CN        | 5.504 | 4.395 | 0.401 | 5.461 | 4.384 | 0.402 | 5.402 | 4.352 | 3.998 | 5.484 | 4.385 | 4.029 |
| SiN       | 7.234 | 5.341 | 7.226 | 7.339 | 5.333 | 4.867 | 7.226 | 5.257 | 4.798 | 7.281 | 5.322 | 4.856 |
| GeN       | 7.831 | 5.645 | 7.578 | 7.823 | 5.625 | 5.136 | 7.578 | 5.488 | 5.011 | 7.744 | 5.610 | 5.129 |
| Ge-N       | 3.626 | 3.612 | 3.569 | 3.600 |
| Diamond   | 3.566 | 3.588 | 3.556 |

1 Ref [26]; 2 Ref [39]. CA-PZ: Ceperly and Alder, parameterized by Perdew and Zunger; PBE: Perdew–Burke–Ernzerhof; PBEsol: Perdew–Burke–Ernzerhof for solids.

**Figure 2.** (a) Lattice parameters and (b) elastic moduli for Pbca-CN/SiN/GeN with PBE level.

### 3.2. Mechanical Properties

The calculated elastic constants and elastic moduli of CN/SiN/GeN in the Pbca phase are listed in Table 2. The calculated elastic constants and elastic modulus of Pbca-CN are excellent agreement with the previous report [26]. For an orthorhombic phase, the criteria of mechanical stability are [45]:

\[
\begin{align*}
\text{for } & i = 1-6, \ C_{11} > 0; \\
\text{for } & i = 1-6, \ C_{ij} > 0, \ j = 1-6; \\
\text{for } & i = 1-6, \ C_{11}C_{22} + C_{12}C_{33} + C_{12}C_{33} + C_{11}C_{33} + 2C_{12}C_{33} &> 0; \\
\text{for } & i = 1-6, \ C_{11}C_{22} - C_{22}C_{33} - C_{11}C_{33} + 2C_{12}C_{33} - C_{12}C_{33} &> 0
\end{align*}
\]

Brittleness and ductility of materials are important properties in crystal physics and engineering sciences. Pugh [48] proposed the ratio of bulk to shear modulus (B/G) as an indication of ductile versus brittle characters. If B/G > 1.75, the material is characterized by a ductile manner; otherwise,
the material has a brittle character. The Poisson’s ratio $v$ is consistent with $B/G$, but refers to brittle compounds, usually with a small $v$ (less than 0.26) [49]. The $B/G$ ratio of Pbca-CN/SiN/GeN is 1.12 (1.11 [26]), 1.63, and 1.70; it is revealed that Pbca-CN/SiN/GeN are all brittle materials, and Pbca-CN has the most brittleness. For Poisson’s ratio $v$, we obtained the same conclusion.

![Figure 3](image_url)

Figure 3. The phonon spectra of (a) Pbca-SiN and (b) Pbca-GeN with PBE level.

Table 2. The calculated elastic constants $C_{ij}$ (in GPa) and bulk moduli $B$ (in GPa), shear moduli $G$ (in GPa), Young’s moduli $E$ (in GPa), and Poisson’s ratio $v$ of Pbca-CN/SiN/GeN and other $C_xN_y$, $Si_xN_y$, and $Ge_xN_y$ compounds with PBE level.

| Materials      | $C_{11}$ | $C_{12}$ | $C_{13}$ | $C_{22}$ | $C_{23}$ | $C_{33}$ | $C_{44}$ | $C_{45}$ | $C_{55}$ | $C_{66}$ | $B$    | $G$    | $E$    | $v$    |
|----------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|-------|-------|-------|-------|
| CN             | 491      | 169      | 139      | 922      | 122      | 1080     | 469      | 307      | 222      | 356      | 319   | 771   | 0.139 |
| CN $^1$        | 495      | 174      | 145      | 934      | 124      | 1112     | 465      | 313      | 243      | 363      | 326   | 754   | 0.154 |
| SiN            | 221      | 107      | 88       | 367      | 90       | 422      | 150      | 75       | 81       | 170      | 104   | 257   | 0.243 |
| SiN$^2$        | 836      |          |          |          |          |          |          |          |          |          |       |       |       |       |
| SiN$^3$        | 442      | 75       | 58       | 610      | 133      | 133      | 237      | 76       | 71       | 191      | 138   | 333   | 0.200 |
| SiN$^4$        | 261      | 97       |          |          |          |          |          |          |          |          | 152   | 73    | 0.290 |
| SiN$^5$        | 581      | 181      | 55       | 587      | 132      | 483      | 244      | 88       | 197      | 262      | 179   | 436   | 0.221 |
| SiN$^6$        | 277      | 152      | 145      |          |          |          |          |          |          |          | 207   | 194   | 311   | 0.233 |
| m-SiN$^7$      | 241      | 39       | 139      | 457      | 55       | 358      | 88       | 128      | 86       | 165      | 104   | 259   | 0.239 |
| GeN            | 159      | 85       | 69       | 243      | 55       | 272      | 107      | 51       | 57       | 119      | 70    | 176   | 0.255 |
| GeN$^3$        | 260      | 40       | 22       | 350      | 94       | 145      | 138      | 45       | 44       | 119      | 85    | 205   | 0.210 |
| m-GeN$^4$      | 203      | 122      | 305      |          |          |          |          |          |          |          |       |       |       |       |
| o-GeN$^5$      | 147      | 87       | 218      |          |          |          |          |          |          |          |       |       |       |       |
| m-GeN$^6$      | 124      | 73       | 183      |          |          |          |          |          |          |          |       |       |       |       |

$^1$Ref [26]; $^2$Ref [18]; $^3$Ref [22]; $^4$Ref [23]; $^5$Ref [46]; $^6$Ref [47].

The Debye temperature ($\Theta_D$) is a fundamental physical property, and correlates with many physical properties of solids (e.g., specific heat and the thermal coefficient) [50]. Debye temperature $\Theta_D$ can be estimated by elastic moduli. The Debye temperature can be estimated from the average sound velocity by the following equation based on elastic constant evaluations [51]: $\Theta_D = (h/k_B)(3npN_A/4\pi M)^{1/3}v_m$, where $h$ is the Planck constant, $k_B$ is Boltzmann’s constant, $n$ is the number of atoms in the molecule, $N_A$ is the Avogadro number, $M$ is the molecular weight, and $\rho$ is the density. The average sound velocity $v_m$ can be calculated as follows: $v_m = [(2/v_1^2 + 1/v_3^2)/3]^{1/3}$, where $v_1 = [(B + 4G/3)/\rho]^{1/2}$, and $v_1 = (G/\rho)^{1/2}$, where $B$ and $G$ are bulk modulus and shear modulus, $v_2$ is the longitudinal sound velocity, and $v_3$ is the transverse sound velocity. In addition, we can obtain the sound velocity in the main directions of a material according to the elastic constants. For the (001) propagation direction in orthorhombic symmetry, polarization direction (001)$v_3 = (C_{33}/\rho)^{1/2}$, (100)$v_1 = (C_{11}/\rho)^{1/2}$, and (010)$v_2 = (C_{44}/\rho)^{1/2}$. For the (010) propagation direction, polarization direction (010)$v_1 = (C_{11}/\rho)^{1/2}$, (100)$v_1 = (C_{11}/\rho)^{1/2}$, and (001)$v_2 = (C_{44}/\rho)^{1/2}$. For the
(100) propagation direction, polarization direction (100)\(v_1 = (C_{11}/\rho)^{1/2}\), (010)\(v_{11} = (C_{66}/\rho)^{1/2}\), and (100)\(v_{22} = (C_{55}/\rho)^{1/2}\) [49,52].

The calculated results of Debye temperature, longitudinal sound velocity, and transverse sound velocity of \(Pbca\)-XN (X = C, Si, Ge) are all listed in Table 3. The densities of \(Pbca\)-XN (X = C, Si, Ge) are also listed in Table 3. For \(Pbca\)-XN (X = C, Si, Ge), in the (001) propagation direction, the (001) polarization direction has the largest sound velocity. The longitudinal sound velocity in the (010) propagation direction aligns with the (001) polarization direction, and the longitudinal sound velocity in the (100) propagation direction aligns with the (010) polarization direction. The longitudinal sound velocity is generally larger than the transverse sound velocity, mainly because the elastic constants that determine the longitudinal sound velocity are greater than those of the transverse sound velocity. In addition, for the same the propagation direction and polarization direction, the sound velocity decreases with X changing from C to Ge. Furthermore, the Debye temperature of \(Pbca\)-XN (X = C, Si, Ge) decreases with X changing from C to Ge. For \(Pbca\)-SiN, the Debye temperature is 863 K; it is slightly smaller than that of \(m\)-\(Si_3N_4\) (892 K), \(o\)-\(Si_3N_4\) (1107 K), and \(t\)-\(Si_3N_4\) (949 K) [53]. The longitudinal sound velocity and transverse sound velocity of \(Pbca\)-XN (X = C, Si, Ge) are different along different directions; this shows that the sound velocity of \(Pbca\)-XN (X = C, Si, Ge) is also anisotropic.

### Table 3. The density (in g/cm³), sound velocities (in m/s), average sound velocity (in m/s), and the Debye temperature (in K) for \(Pbca\)-CN/SiN/GeN with PBE level.

| Materials | CN | SiN | GeN |
|-----------|----|-----|-----|
| \(\rho\)  | 3.536 | 2.922 | 5.039 |
| (100)\(v_1\) | 11,784 | 8697 | 5617 |
| (010)\(v_{11}\) | 7927 | 5265 | 3363 |
| (001)\(v_{12}\) | 9318 | 5066 | 3181 |
| (010)\(v_1\) | 16,148 | 11,207 | 6944 |
| (100)\(v_{11}\) | 7927 | 5265 | 3363 |
| (001)\(v_{12}\) | 11,517 | 7165 | 4608 |
| (001)\(v_1\) | 17,477 | 12,018 | 7347 |
| (100)\(v_{11}\) | 9318 | 5066 | 3181 |
| (010)\(v_{12}\) | 11,517 | 7165 | 4608 |
| \(v_l\) | 14,865 | 10,278 | 6491 |
| \(v_t\) | 9498 | 5966 | 3727 |
| \(v_m\) | 10,437 | 6620 | 4140 |
| \(\Theta_D\) | 1702 | 863 | 508 |

### 3.3. Electronic Properties

In solid-state physics and semiconductor physics, the band structure of a solid or a material describes the energy that is forbidden or permitted by electrons. The band structure of a material determines a variety of properties—especially its electronic and optical properties. It is known that since the calculated band gap with DFT is usually underestimated by 30–50%, the band gap should be greater than the calculated results with the PBE functional. Hence, the band structures of \(Pbca\)-CN/SiN/GeN calculated utilizing the Heyd–Scuseria–Ernzerhof (HSE06) [37,38] hybrid functional are shown in Figure 4a–c, respectively. The band gap of \(Pbca\)-CN is 5.41 eV within the HSE06 hybrid functional and 3.96 eV within the PBE functional; the results of the PBE functional of \(Pbca\)-CN are in excellent agreement with previous report [26]. The valence band maximum is located at the G point in the Brillouin zone, whereas the conduction band minimum is located at the X point. That is to say, \(Pbca\)-CN is an indirect semiconductor with a band gap of 3.94 eV. In contrast, the valence band maximums of \(Pbca\)-SiN and \(Pbca\)-GeN are all located at the G point in the Brillouin zone; it is shown that \(Pbca\)-SiN and \(Pbca\)-GeN are both direct semiconductors with band gaps of 3.39 eV and 2.22 eV, respectively. In addition, the Fermi level decreases as the carbon atoms change into silicon atoms; the silicon atoms then change into germanium atoms, and the Fermi level also decreases. Similar to the lattice constants and the elastic moduli, the Fermi level changes rapidly when the carbon
atom is replaced by silicon atoms. The Fermi levels of Pbca-CN/SiN/GeN are 11.02 eV, 2.26 eV, and 0.01 eV, respectively.

![Figure 4](image)

**Figure 4.** The band structures of (a) Pbca-CN; (b) Pbca-SiN; and (c) Pbca-CN GeN with the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional with PBE level.

### 3.4. Elastic Anisotropy Properties

The elastic anisotropy properties are an important characteristic of materials. Along the different crystallographic directions, various elastic moduli exhibit different values. In this work, we mainly investigated the anisotropy of Poisson’s ratio $\nu$, shear modulus, bulk modulus, and Young’s modulus in different planes and different directions. The Poisson’s ratio $\nu$ and shear modulus $\mu$ have two unit vectors ($a$, $b$) and three angles $[43,54]$, so they have a maximum value and a minimum value in the same direction, while the Young’s modulus has only two unit vectors ($a$, $b$) and a two-angle description $[43,54]$, so it is in the same direction with only one value. The Poisson’s ratio $\nu$ of Pbca-CN/SiN/GeN in the (001) plane (namely the $xy$ or $ab$ plane), the (010) plane (namely the $xz$ or $ac$ plane), and the (100) plane (namely the $yz$ or $bc$ plane) are displayed in Figure 5a–c, respectively. From Figure 5a–c, it is obvious that the Poisson’s ratio $\nu$ of Pbca-CN/SiN/GeN exhibits a larger anisotropy. In the (001), (010), and (100) plane, along almost all directions, the Pbca-GeN exhibits the largest Poisson ratio. The positions of the maximum values are all located at $\theta = 1.57$, $\phi = 4.73$ (more details see $[43,54]$) for Pbca-CN/SiN/GeN; the angles $\theta$ and $\phi$ are measured in radians. The minimum values of Pbca-CN/SiN/GeN occupy the position $\theta = 2.33$, $\phi = 1.87$; $\theta = 1.46$, $\phi = 1.06$; and $\theta = 0.83$, $\phi = 4.73$, respectively.

The shear moduli $G$ of Pbca-CN/SiN/GeN in the (001), (010), and (100) planes are displayed in Figure 6a–c, respectively. The cyan line, red line, and blue line represent the Poisson’s ratio...
The Poisson’s ratio \(\nu\) of Pbca-CN/SiN/GeN in Figure 6, and the dashed line and solid line represent the maximum value and minimum value of the shear modulus, respectively. The maximum shear moduli \(G\) of Pbca-CN/SiN/GeN are 469 GPa, 150 GPa, and 107 GPa, and the minimum shear moduli of Pbca-CN/SiN/GeN are 379 GPa, 106 GPa and 74 GPa, respectively. From Figure 6a,c, with X change from C to Ge, the shape of the minimum value for shear modulus is increasingly rounded in the (001) plane and (100) plane, while in the (010) plane the shape of the minimum is closer to a square. The ratios \(G_{\text{max}}/G_{\text{min}}\) of Pbca-CN/SiN/GeN are 1.24, 1.42, and 1.53; in other words, the elastic anisotropy in shear modulus becomes larger and larger with X changing from C to Ge.

\[ \begin{align*}
(a) \ (001) \text{ plane} & & & & (b) \ (010) \text{ plane} \\
\end{align*} \]

Figure 5. The two-dimensional representation of Poisson’s ratio in the (a) (001) plane; (b) (010) plane; and (c) (100) plane for Pbca-CN/SiN/GeN with PBE level. The cyan line, red line, and blue line represent the Poisson’s ratio \(\nu\) of Pbca-CN/SiN/GeN, respectively.

\[ \begin{align*}
(a) \ (001) \text{ plane} & & & & (b) \ (010) \text{ plane} \\
\end{align*} \]

Figure 6. Cont.
Young’s modulus is a measure of the stiffness of a solid material. It is a mechanical property of linear elastic solid materials. It defines the relationship between stress (force per unit area) and strain (proportional deformation) in a material. To study the elastic anisotropy in more detail, a variation of Young’s modulus with crystallographic direction is displayed in a three-dimensional manner. The directional dependence of Young’s modulus $E$ for orthorhombic crystal is [55]:

$$ E^{-1} = l_1^2 S_{11} + l_2^2 S_{22} + l_3^2 S_{33} + 2l_1^2 l_2 S_{12} + 2l_1^2 l_3 S_{13} + 2l_2^2 l_3 S_{23} + l_1^2 S_{44} + l_3^2 S_{55} + l_2^3 S_{66}, $$

where $l_1$, $l_2$, and $l_3$ are the direct cosines of the $uvw$ direction, and $S_{ij}$ refers to the elastic compliance constants. The three-dimensional surface representations of Young’s modulus $E$ for Pbca-CN/SiN/GeN are illustrated in Figure 7a–c.

For an isotropic system, the three-dimensional directional dependence exhibits a spherical shape. If there is a deviation of degrees from the spherical shape, it reflects the material exhibiting elastic anisotropy [56]. From Figure 7a–c, it is obvious that the shape of the three-dimensional directional dependence does not exhibit a spherical shape, and the shapes of the three-dimensional directional dependence for Pbca-CN/SiN/GeN all exhibit mechanical anisotropy in Young’s modulus.

To further understand the elastic anisotropy of the Young’s modulus along different directions, the dependence of the Young’s modulus on orientation is investigated when we take the tensile axis within a given plane. Let $\alpha$ be the angle of between (100) and $(uvw)$ for the (001) plane; the Young’s modulus between (100) and $(uvw)$ for the (001) plane can be expressed as:

$$ E^{-1} = S_{11}\cos^4\alpha + S_{22}\sin^4\alpha + 2S_{12}\sin^2\alpha\cos^2\alpha + S_{44}\sin^2\alpha\cos^2\alpha. $$

Let $\beta$ be the angle of between (001) and $(uvw)$ for the (010) plane; the Young’s modulus between (001) and $(uvw)$ for the (010) plane can be calculated as:

$$ E^{-1} = S_{11}\sin^4\beta + S_{33}\cos^4\beta + (2S_{13}\sin^22\beta + S_{55}\sin^22\beta)/4. $$

Let $\gamma$ be the angle of between (001) and $(0vw)$ for the (001) plane, the Young’s modulus between (001) and $(0vw)$ for the (001) plane can be estimated as:

$$ E^{-1} = S_{22}\sin^4\gamma + S_{33}\cos^4\gamma + (2S_{23}\sin^22\gamma + S_{44}\sin^22\gamma)/4. $$

The two-dimensional representations of Young’s modulus in the (001) plane, (010) plane, and (100) plane for Pbca-CN/SiN/GeN are illustrated in Figure 7d–f, respectively. The cyan line, red line, and blue line represent the Poisson’s ratio $\nu$ of Pbca-CN/SiN/GeN, respectively. From Figure 7d–f, the (001) plane and (010) plane of Pbca-CN/SiN/GeN exhibit a larger elastic anisotropy in Young’s modulus than the (100) plane. Pbca-CN has a maximum of $E_{\text{max}} = 1034$ GPa and a minimum of $E_{\text{min}} = 447$ GPa. The calculated results of elastic anisotropy in Young’s modulus for Pbca-CN are in excellent agreement with [26]. Pbca-CN/SiN/GeN has a maximum of $E_{\text{max}} = 380/241$ GPa and a minimum of $E_{\text{min}} = 179/120$ GPa. In order to quantify the elastic anisotropy, we introduce a ratio; that is, the ratio of the maximum and minimum Young’s modulus (ratio $E_{\text{max}}/E_{\text{min}}$). The greater the ratio $E_{\text{max}}/E_{\text{min}}$, the greater the maximum and minimum differences, and the greater the anisotropy of the material. Through the values of the ratio $E_{\text{max}}/E_{\text{min}} = 2.31, 2.12$, and 2.01, it is shown that the elastic anisotropy in Young’s modulus for Pbca-XN (X = C, Si, Ge) decreases with X changing from C to Ge. In addition, the maximum values of Pbca-CN/SiN/GeN all occupy the position $\theta = 0, \phi = 0$; that is, the maximum values of Pbca-XN...
(X = C, Si, Ge) all occupy the z (c) axis, while the minimum values of Pbca-CN/SiN/GeN do not occupy the same position (x (a) axis). The minimum value of Pbca-SiN is located at $\theta = 1.32$, $\phi = 0$, but the minimum value of Pbca-CN/GeN occupies the position of $\theta = \pi/2$, $\phi = 0$. For the orthorhombic phase, the dependence of the bulk modulus $B$ along the crystallographic direction is expressed by:

$$B^{-1} = (S_{11} + S_{12} + S_{13})l_1 + (S_{12} + S_{22} + S_{23})l_2 + (S_{13} + S_{23} + S_{33})l_3.$$  

The three-dimensional surface representations of bulk modulus $B$ for Pbca-CN/SiN/GeN are illustrated in Figure 8a–c. The anisotropy of the bulk modulus of Pbca-XN (X = C, Si, Ge) is similar to that of Young’s modulus; the (001) plane and (010) plane of Pbca-CN/SiN/GeN exhibit a larger elastic anisotropy in bulk modulus than the (100) plane.

![Figure 7](image-url)  

Figure 7. The surface constructions of Young’s modulus for (a) Pbca-CN; (b) Pbca-SiN; and (c) Pbca-GeN with PBE level. Two-dimensional representation of Young’s modulus in the (d) (001) plane; (e) (010) plane; and (f) (100) plane for Pbca-CN/SiN/GeN with PBE level. The cyan line, red line, and blue line represent the Poisson’s ratio $\nu$ of Pbca-CN/SiN/GeN, respectively.
The Debye temperature, longitudinal sound velocities, and transverse sound velocities are also estimated using the elastic constants. The elastic anisotropy calculations showed that Pbca\textsubscript{Si}, Pbca\textsubscript{Ge}, Pbca\textsubscript{SiN}, Pbca\textsubscript{GeN}, and Pbca\textsubscript{CN} have anisotropy in bulk modulus, shear modulus, Poisson’s ratio, Young’s modulus, and sound velocities. The structural, mechanical, electronic, and elastic anisotropy properties of CN, SiN, and GeN in orthorhombic phase were performed using DFT calculations in this work. SiN and GeN are mechanically and dynamically stable, fulfilling the Born stability criteria for an orthorhombic phase. Furthermore, for Pbca-CN, the universal anisotropic index is slightly smaller than that of Pbca-Si3N4 (0.968), while it is much higher than that of Pbca-C3N4 (0.798). The universal anisotropic index of Pbca-SiN is slightly larger than that of Pbca-C3N4 (0.717), but it is smaller than that of Pbca-C3N4 (0.582) and Pbca-Si3N4 (1.231).

4. Conclusions

The structural, mechanical, electronic, and elastic anisotropy properties of CN, SiN, and GeN in orthorhombic phase were performed using DFT calculations in this work. SiN and GeN are mechanically and dynamically stable, fulfilling the Born stability criteria for an orthorhombic phase and phonon spectra, respectively. PBE function predicts lattice parameters that agree well with the previous report. From band gap calculations with the HSE06 function, SiN and GeN are direct band gap semiconductor materials with band gap of 3.39 eV and 2.22 eV, while CN has an indirect band gap with band gap of 5.41 eV. The elastic moduli of Pbca-XN (X = C, Si, Ge) such as Young’s moduli, bulk moduli, shear moduli, Poisson’s ratio, and sound velocities have also been reported in this work. The Debye temperature, longitudinal sound velocities, and transverse sound velocities are also estimated using the elastic constants. The elastic anisotropy calculations showed that Pbca-XN (X = C, Si, Ge) exhibited anisotropy in bulk modulus, shear modulus, Poisson’s ratio, Young’s modulus, and

Figure 8. The surface constructions of bulk modulus in the (a) (001) plane; (b) (010) plane; and (c) (100) plane for Pbca-CN/SiN/GeN with PBE level.
A^U. Besides, the elastic anisotropy in bulk modulus, shear modulus, Poisson’s ratio, Young’s modulus, and A^U for Phca-XN (X = C, Si, Ge) decreases with X changing from C to Ge.

Acknowledgments: This work was supported by the Natural Science Foundation of China (No. 61601468), the Fundamental Research Funds for the Central Universities (No. 3122014C024), and the Fund for Scholars of Civil Aviation University of China (No. 2013QD06X). Q.Y. FAN (School of Microelectronics, Xidian University) is thanked for allowing to use the CASTEP code in Materials Studio.

Author Contributions: Zhenyang Ma and Xuhong Liu designed the project; Zhenyang Ma, Xuhong Liu, Qingynag Fan, and Dayun Wang performed the calculations; Zhenyang Ma, Xuhong Liu, Xinhai Yu, and Chunlei Shi determined the results; Zhenyang Ma and Xuhong Liu wrote the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

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