

## Interesting Physical Properties of the New Spinel Phase of $\text{Si}_3\text{N}_4$ and $\text{C}_3\text{N}_4$

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The physical properties of the new high-pressure spinel phase of  $\text{Si}_3\text{N}_4$  and  $\text{C}_3\text{N}_4$  were studied by first-principles calculations. The presence of Si at the octahedral site and the elongated Si-N bonds under pressure have a profound effect on many properties of  $\text{Si}_3\text{N}_4$  including lowering the compressibility, decreasing the direct band gap and effective mass, increasing the static dielectric constants, and enhancing covalent bonding. The last effect is explained by calculating the bond order and number of bonds. Possible routes of synthesis at lower pressure and potential applications are suggested.

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$\text{Si}_3\text{N}_4$  is an important structural ceramic with many applications because of its outstanding high temperature and oxidation resistant properties. Two stable phases of  $\text{Si}_3\text{N}_4$ ,  $\alpha$  and  $\beta$  have thus far been synthesized. Both crystals have a hexagonal crystal structure in which all Si is tetrahedrally bonded to N atoms with a strong covalent character. Recently, it was reported that a third phase of  $\text{Si}_3\text{N}_4$  in the cubic spinel phase ( $c\text{-Si}_3\text{N}_4$ ) could be synthesized under high pressure above 15 GPa and at a temperature exceeding 2000 K [1]. The spinel phase is a major class of oxides with a chemical formula  $AB_2O_4$  where  $A$  and  $B$  are the tetrahedral (tet) and octahedral (oct) cation sites. This new phase is particularly significant for  $\text{Si}_3\text{N}_4$  since for the first time Si is found to have an octahedral coordination with N in a pure binary compound. The cubic structure can induce a different electronic band structure with drastically altered physical properties that may lead to new applications. It is therefore timely to investigate the physical properties of  $c\text{-Si}_3\text{N}_4$ .

The existence of  $c\text{-Si}_3\text{N}_4$  naturally leads to the speculation that  $\text{C}_3\text{N}_4$  may also exist in the spinel phase.  $\text{C}_3\text{N}_4$  has been suggested as a superhard material with a bulk modulus exceeding or comparable to that of diamond [2]. Over the last few years, there have been overwhelming research activities to synthesize and search for  $\text{C}_3\text{N}_4$  [3–13]. There are reports that the hexagonal  $\beta\text{-C}_3\text{N}_4$  has been detected or synthesized [5,6,8,12,13]. However, conclusive evidence has yet to be provided. Using theoretical calculation as the tool, Teter and Hemley have explored several possible tetrahedrally coordinated polymorphs of  $\text{C}_3\text{N}_4$  that may have a low compressibility [3]. They found that  $\alpha\text{-C}_3\text{N}_4$  and graphite- $\text{C}_3\text{N}_4$  are energetically favorable to  $\beta\text{-C}_3\text{N}_4$  and that a cubic phase with a willemite-II structure and  $I\text{-}43d$  symmetry

may have a zero-pressure bulk modulus exceeding that of diamond. They did not explore the spinel phase, presumably assuming that an octahedral coordination of C with N is impossible. It is very likely that the cubic spinel phase of  $\text{C}_3\text{N}_4$  ( $c\text{-C}_3\text{N}_4$ ) may be synthesized at high temperature and pressure similar to  $c\text{-Si}_3\text{N}_4$ , and its physical properties will be of great interest.

In this Letter, we report detailed *ab initio* calculations of the physical properties of  $c\text{-Si}_3\text{N}_4$  and  $c\text{-C}_3\text{N}_4$ . The results include equilibrium crystal structures, band structures, density of states (DOS), Mulliken charges, bond order, number of bonds, optical properties, bulk moduli  $B$  and the pressure coefficients  $B'$ , and the transition pressure from the  $\beta\text{-Si}_3\text{N}_4$  to  $c\text{-Si}_3\text{N}_4$ . These results enable us to understand the nature of electronic bonding in  $c\text{-Si}_3\text{N}_4$  and to propose possible routes to synthesize it at a lower transition pressure. We also suggest potential applications for the new material.

We have used the first-principles orthogonalized linear combinations of atomic orbitals method (OLCAO) to calculate the total energy (TE) and the electronic structures of the  $c\text{-Si}_3\text{N}_4$  and  $c\text{-C}_3\text{N}_4$ . The OLCAO is a density-functional theory-based method with a local approximation for the exchange-correlation interaction or the so-called local density approximation (LDA). The method is known for its accuracy and efficiency, especially for materials with complex structure [14]. In the present calculations, a full basis expansion including additional unoccupied orbitals of Si and N was used. Ten special  $k$ -points in the irreducible wedge of the Brillouin zone (BZ) were used which were sufficient for convergence in the TE calculation. With a basis consisting of atomic orbitals, the interpretation of the electronic structure is rather straightforward. Mulliken effective charge

and bond order calculations (in a separate minimal basis calculation) provide useful insight on the nature of electronic bonding in these crystals. The optical property calculation involves the evaluation of transition matrix elements at a large number of  $k$  points in the BZ (162 in the present case).

We have recently implemented an efficient scheme for crystal geometry optimization without direct calculation of forces on individual atom [15]. Partial derivatives of the TE with respect to each crystal parameter were evaluated numerically. This scheme enables us to optimize the lattice constants and internal parameters of a given crystal using the TE data. The volume dependence of the TE can be obtained with all internal parameters optimized. When applied to  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$ , the equilibrium lattice constants are within 0.5% from the measured ones [15].

The calculated results for  $c$ - $\text{Si}_3\text{N}_4$  and the hypothetical  $c$ - $\text{C}_3\text{N}_4$  are summarized in Table I. The band structures of  $c$ - $\text{Si}_3\text{N}_4$  and  $c$ - $\text{C}_3\text{N}_4$  are shown in Fig. 1. We will concentrate our discussion on  $c$ - $\text{Si}_3\text{N}_4$ . The calculated equilibrium lattice constant for  $c$ - $\text{Si}_3\text{N}_4$  is 7.837 Å, which is in excellent agreement with the measured value of  $7.80 \pm 0.03$  Å [1]. The internal parameters for the  $N$  position,  $x$ , are found to be 0.3843 ( $\delta = 0.0123$ ) [16]. The direct band gap of 3.45 eV at  $\Gamma$  is much smaller than the band gap of  $\beta$ - $\text{Si}_3\text{N}_4$  (indirect: 4.96 eV, direct: 5.25 eV) calculated using the same method [17]. The calculated band gap for  $c$ - $\text{C}_3\text{N}_4$  is even smaller, 1.14 eV, and is significantly smaller than the gap of 3.56 eV for  $\beta$ - $\text{C}_3\text{N}_4$ . Since the LDA calculation generally underestimates the true band gap, this puts  $c$ - $\text{Si}_3\text{N}_4$  in the class of wide-gap semiconductors, rather than a large gap insulator. The directionally averaged effective mass at the conduction band (CB) edges is 0.51, while the top of the valence band (VB) is very flat. The relatively small electron

TABLE I. Calculated physical properties of the spinel phase of  $\text{Si}_3\text{N}_4$  and  $\text{C}_3\text{N}_4$ .

	$c$ - $\text{Si}_3\text{N}_4$	$c$ - $\text{C}_3\text{N}_4$
$a$ (Å)	7.8367	6.8702
$x$	0.3843	0.3818
$\rho$ (g/cm <sup>3</sup> )	3.873	3.772
$E_g$ (eV)	3.45	1.14
VB width (eV)	10.25, 5.32	23.8
$m^*/m$ (top of VB)	Large	-0.45
$m^*/m$ (bottom of CB)	0.51	4.25
$Q^*$ (electron)		
Si or C(tet)	2.63	3.69
Si or C(oct)	2.54	3.64
N	6.05	5.26
Bond order $\rho_{ij}$		
Si or C(tet)-N	0.362 (1.830 Å)	0.358 (1.585 Å)
Si or C(oct)-N	0.242 (1.885 Å)	0.241 (1.676 Å)
$\epsilon_0$	4.7	7.7
$B$ (Gpa)	280	369
$B'$	3.48	3.85

effective mass means potential application of  $c$ - $\text{Si}_3\text{N}_4$  as a semiconductor. This favorable property near the band gap is due to the cubic structure and the presence of octahedrally bonded Si, or Si(oct) (see explanation below). The total DOS and the site-decomposed partial DOS (PDOS) for  $c$ - $\text{Si}_3\text{N}_4$  are shown in Fig. 2. Comparing with those of  $\beta$ - $\text{Si}_3\text{N}_4$ ,  $c$ - $\text{Si}_3\text{N}_4$  has a smaller band gap, a steeper VB edge, and a less sharp CB edge.  $\beta$ - $\text{Si}_3\text{N}_4$  and  $c$ - $\text{Si}_3\text{N}_4$  also have different multiple structures in the DOS in both the VB and CB regions. In particular, we note the different peak positions in the PDOS of Si(tet) and Si(oct). Si(oct) has a much gentler slope near the CB edge than Si(tet). Such a difference should be easily detected by energy loss near edge spectroscopy (ELNES) or x-ray absorption near-edge spectroscopy (XANES). In the  $\text{Y}_3\text{Al}_5\text{O}_{12}$  (YAG) crystal, Al also occupies both tetrahedral and octahedral sites. The difference in the orbital-resolved PDOS at different sites can explain the measured Al-K and Al-L edges quite well [18].

The calculated Mulliken effective charges  $Q^*$  for Si(tet), Si(oct), and N in  $c$ - $\text{Si}_3\text{N}_4$  are 2.63, 2.54, and 6.05, respectively. This is to be compared with the  $Q^*$  of 2.50 for Si and 6.13 for N in  $\beta$ - $\text{Si}_3\text{N}_4$  [17]. Thus, the high-pressure cubic phase is more covalent than the  $\beta$  phase. This is similar to the case of  $\text{SiO}_2$  in which the high-pressure stishovite phase is much more covalent than the low-pressure phase quartz. The bond order  $\rho_{ij}$  between a pair of atoms  $i$  and  $j$  is a measure of the strength of the bond. It can be calculated from the overlap integrals between the Bloch functions with an atomic basis expansion. The calculated values are 0.362 for Si(tet)-N with a bond length (BL) of 1.830 Å, and 0.242 for Si(oct)-N (BL = 1.885 Å). This is to be compared with the bond order values ranging from 0.314 to 0.339 for BL of 1.738, 1.725, and 1.748 Å in  $\beta$ - $\text{Si}_3\text{N}_4$ . The number of Si-N, Si-Si, and N-N bonds per  $\text{Si}_3\text{N}_4$  molecular unit are illustrated in Fig. 3. The total bond order of the crystal can be obtained by multiplying the individual bond order by the number of bonds per molecular unit. It is found to be 7.68 for  $\beta$ - $\text{Si}_3\text{N}_4$  and 8.70 for

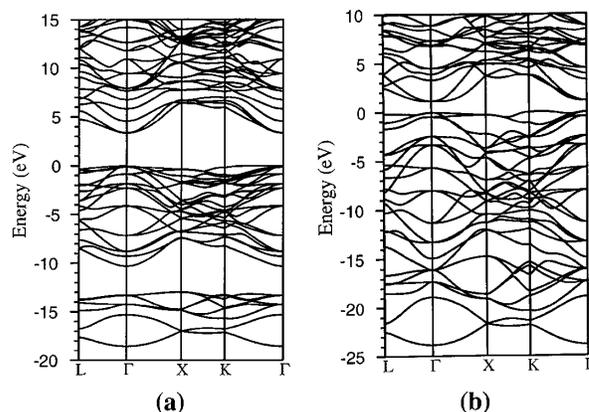


FIG. 1. Calculated band structure of: (a)  $c$ - $\text{Si}_3\text{N}_4$ ; (b)  $c$ - $\text{C}_3\text{N}_4$ .

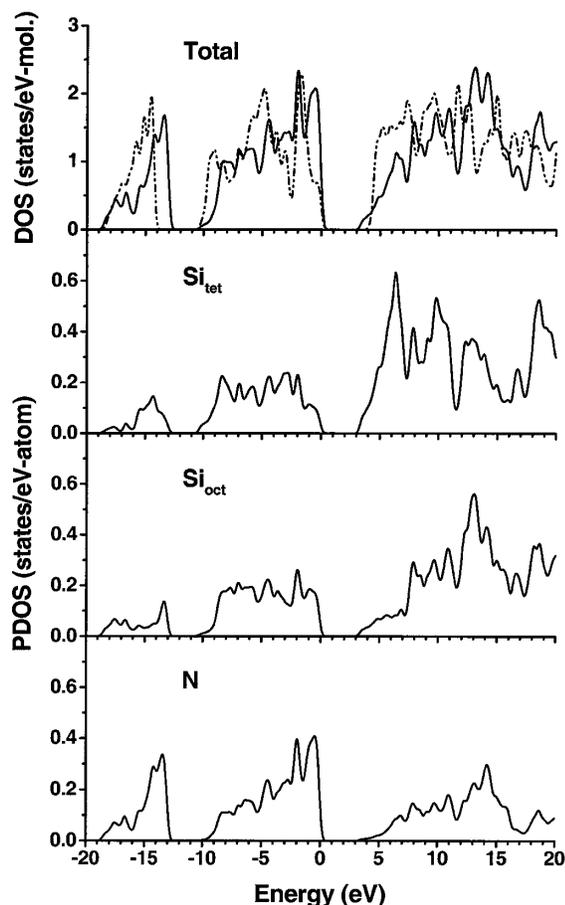


FIG. 2. Calculated total and partial DOS of  $c$ - $\text{Si}_3\text{N}_4$ . The dashed line is the total DOS for  $\beta$ - $\text{Si}_3\text{N}_4$ .

$c$ - $\text{Si}_3\text{N}_4$ . Thus  $c$ - $\text{Si}_3\text{N}_4$  is much more covalent. The amazing part is that in going from  $\beta$ - $\text{Si}_3\text{N}_4$  to  $c$ - $\text{Si}_3\text{N}_4$ , the SiN BLs are actually increased by 6–9%, while the volume is reduced by 17%. The shortest Si-Si and N-N bonds in  $c$ - $\text{Si}_3\text{N}_4$  are both decreased. In  $\beta$ - $\text{Si}_3\text{N}_4$ , there exists a large open channel along the  $c$  axis. This open space is destroyed by pressure, causing the number of Si-N and Si-Si bonds to increase. The shortest Si-Si bond is only 2.77 Å, which could determine the shape of the bottom of the CB. On the other hand, the N-N bond does not increase that much upon compression since N atoms are already closely packed in  $\beta$ - $\text{Si}_3\text{N}_4$  due to its large ionic radius.

The calculated TE vs volume ( $V$ ) data were fitted to three types of equation of states (EOS), the Murnaghan, Birch, and fourth order polynomial expansion. The  $B$  values of 280 Gpa from the three EOS fits are almost the same. The Murnaghan EOS has the smallest rms deviation of fitting (0.00027 for eight data points), and gives a pressure coefficient  $B' = 3.48$ . From the slope of a common tangent construct to the  $E$  vs  $V$  curves for  $c$ - $\text{Si}_3\text{N}_4$  and  $\beta$ - $\text{Si}_3\text{N}_4$ , we obtained a transition pressure  $P_T$  of 38 GPa which is higher than the reported transition

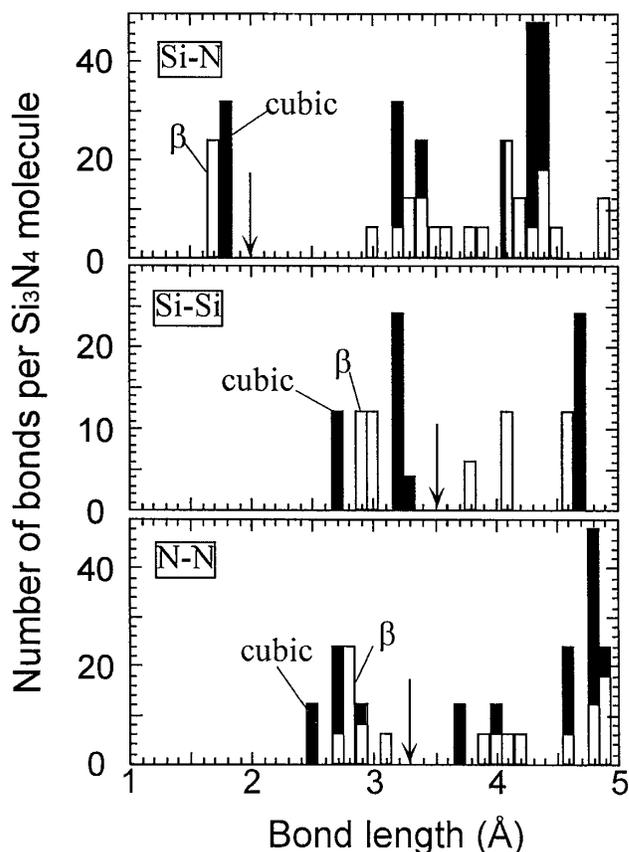


FIG. 3. Number of bonds per molecular unit in the two  $\text{Si}_3\text{N}_4$  crystals. The arrows indicate the boundary (arbitrarily chosen) between the first near-neighbor shell and the other. The number of bonds within the first nearest-neighbor shell are (24, 32) for Si-N, (24, 40) for Si-Si, and (44, 48) for N-N. The first (second) number in parenthesis is for  $\beta$ - $\text{Si}_3\text{N}_4$  ( $c$ - $\text{Si}_3\text{N}_4$ ).

pressure of 15–30 GPa [1]. A similar LDA calculation using the plane-wave pseudopotential method gives a  $P_T$  of 13 GPa [1]. For  $c$ - $\text{C}_3\text{N}_4$ , the calculated  $B$  reaches a high value of 369 Gpa, which rivals that of diamond and is comparable to  $c$ -BN. Since the spinel phase of the  $\text{Si}_3\text{N}_4$  has been synthesized, it is highly likely that the spinel phase for  $\text{C}_3\text{N}_4$  with a low compressibility can also be obtained using the ultra-high-pressure technique.

The optical properties of  $c$ - $\text{Si}_3\text{N}_4$  and  $c$ - $\text{C}_3\text{N}_4$  were also calculated. The procedure is the same as similar calculations for the  $\beta$ - $\text{Si}_3\text{N}_4$  and  $\alpha$ - $\text{Si}_3\text{N}_4$  [17], and  $\beta$ - $\text{C}_3\text{N}_4$  [7]. A large number of  $k$  points in the BZ were used, and the dipole transition matrix elements between VB and CB were all included. The calculated dielectric functions for  $c$ - $\text{Si}_3\text{N}_4$  and  $c$ - $\text{C}_3\text{N}_4$  are shown in Fig. 4. The major absorption peak is at 10 and 6.5 eV, respectively. These complex dielectric functions are quite different from those of the respective  $\beta$  phases [7,17]. The static dielectric constant  $\epsilon(0)$  is obtained as the zero frequency limit of the real part of the frequency-dependent dielectric function. The calculated  $\epsilon(0)$  is 4.70 for  $\beta$ - $\text{Si}_3\text{N}_4$  and 7.7 for  $c$ - $\text{C}_3\text{N}_4$ ; both are larger than the  $\epsilon(0)$  for the respective  $\beta$  phases.

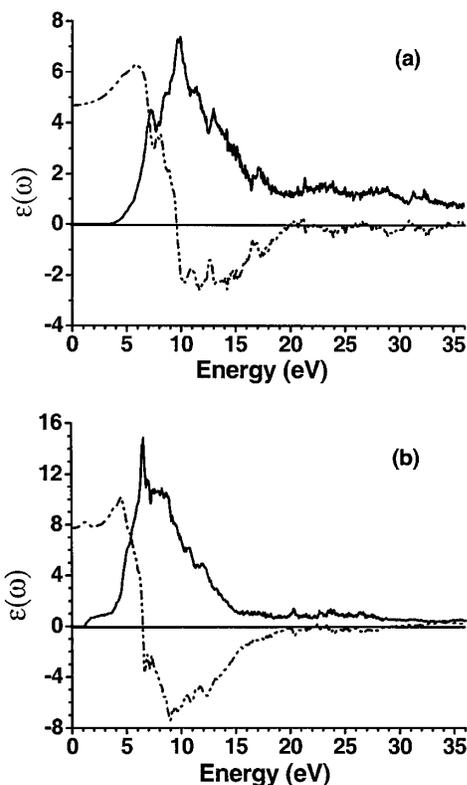


FIG. 4. Calculated frequency-dependent dielectric function of: (a)  $c$ - $\text{Si}_3\text{N}_4$ ; (b)  $c$ - $\text{C}_3\text{N}_4$ . The solid (dashed) line is for the impaginary (real) part.

A larger  $\epsilon(0)$  means a larger refractive index. A higher optical density for the spinel phase may have special applications in certain optical components.

The real challenge for realistic applications of the spinel phases of  $\text{Si}_3\text{N}_4$  or  $\text{C}_3\text{N}_4$  is to be able to synthesize these phases at a lower pressure. This may be achieved by choosing optimum substrate for epitaxial growth of thin films. An alternative route may be chosen by careful selection of suitable solutes, which can stabilize the cubic phase at a lower pressure. The most likely candidates will be Ge or Ti. Ge and Ti both have ionic radii larger than Si, and therefore can induce internal pressure because of the larger size. Also, TiN exists in the rocksalt structure, and there is evidence that the spinel phase of  $\text{Ge}_3\text{N}_4$  may also exist [1]. So it is possible that the inclusion of Ti or Ge may stabilize the  $c$ - $\text{Si}_3\text{N}_4$  structure. It is also conceivable that spinel phase involving both Si and C may be synthesized. Assuming the physical properties of such solid solutions are not different from the high pressure phase of  $c$ - $\text{Si}_3\text{N}_4$  and  $c$ - $\text{C}_3\text{N}_4$ , then real and new applications of  $c$ - $\text{Si}_3\text{N}_4$  and related materials can be realized, especially in the area of wear-resistant high temperature cutting tools which command a significant market in the industry. Another potential application is

as a candidate for violet or ultraviolet laser materials or as light emitting diodes because of the favorable direct band gap. Preliminary calculation by us indicates that the LDA gap of  $c$ - $\text{CSi}_2\text{N}_4$  in the spinel structure is about 1.76 eV, intermediate between those of  $c$ - $\text{Si}_3\text{N}_4$  and  $c$ - $\text{C}_3\text{N}_4$ . It is possible that a direct band gap of desirable size can be engineered by appropriate mixing.

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