Potential ultrahard nitride materials containing silicon, carbon and nitrogen

J. E. Lowther,[1] M. Amkreutz,[2] Th. Frauenheim,[2] E. Kroke,[3] and R. Riedel[3]

[1]*School of Physics, University of Witwatersrand, Johannesburg, South Africa*
[2]*Department of Physics, Theoretical Physics, University of Paderborn, 33098 Paderborn, Germany*
[3]*Fachbereich Disperse Feststoffe, Technische Universität Darmstadt, Fachbereich Material- und Geowissenschaften,*
Petersenstrasse 23, 64287 Darmstadt, Germany

Using *ab initio* and self-consistent-charge density functional based tight-binding electronic structure calculations the possibility that a recently synthesized layered structure of Si_2CN_4 can lead to superhard structures in the spinel or the β phase is discussed. Both methods show that extensive compression of the layered phase leads to an abrupt breakdown of the N-C-N bonds. The compressed volume at which this occurs is above the volume belonging to the predicted transition pressures at which the layered phase and β phases can coexist simultaneously. Kinetic factors are important in all cases.

Carbon remains the most important element as a base for materials with major refractory properties and diamond still prevails as being the hardest known material. Recently advanced nitrides—and especially silicon nitrides—have proven to be of use as engineering ceramics with Si_3N_4 being the prototype material leading to the postulate that carbon nitride in the form C_3N_4 may be harder than diamond.[1,2] More recently a variety of other structures involving Si, C, and N have been suggested[3–5] as having potentially superhard properties.

Silicon nitride in the form Si_3N_4 is expected to take either the α or β hexagonal forms although recently yet another higher density structure has been identified[6] with a cubic spinel structure. A similar spinel structure has been observed for the binary Ge_3N_4 system.[7] In this structure either the Ge or Si atom is in octahedral coordination by six N atoms and simultaneously in tetrahedral coordination by four N atoms. Several modifications of these structures have now been theoretically considered when C replaces Si or Ge atoms in the conventional Si_3N_4 structures.[3–5] It has been found that the elastic properties—as measured by a bulk modulus— vary within a specified structure and also show a strong dependence upon C content.[3] The possible incorporation of C into the Si_3N_4 material is expected to considerably enhance the potential as an ultrahard material.[8]

In this paper we examine properties of potential Si_2CN_4 phases. Structural forms are derived using *ab initio* plane wave techniques as are the various bulk moduli. For the $Aba2$ phase also a self-consistent-charge density functional based tight-binding (SCC-DFTB) method is applied for structure calculations especially under compression and determination of the bulk modulus. Throughout, our results demonstrate the importance of the C-N bond in these materials. We consider the layered form of Si_2CN_4 that has been suggested as a possible precursor[9] and how this may lead to ultra hard phases. Our results show that the strength of the C-N bond that connects the layers in this material may not be a major hindrance for its use as a possible precursor phase as thought earlier. We find that under extreme compression the C-N bond will significantly deform. The conditions under which this bond effectively collapses is also consistent with

the predicted synthesis pressure on the $Aba2$ phase that leads to either the β or spinel structures.

The relative stability of the various phase as well as their elastic properties have been investigated using techniques of *ab initio* molecular dynamics with soft Troullier-Martin[10] pseudopotentials. The structures were optimized using a plane wave algorithm[11] and the energy-volume results fitted to a standard equation of state[12] from which an estimate of the bulk modulus can be obtained. Each structure was completely optimized for a specified cell geometry with lattice relaxation of all atoms included. This procedure is proving to be quite reliable in the computational design of advanced materials.

In addition to the plane wave method described above, the self-consistent-charge density-functional based tight-binding (SCC-DFTB) method as described in detail elsewhere[13–15] has been used to investigate the precursor $Aba2$ phase with a periodic supercell containing 252 atoms. The energetically favored structure for the $Aba2$ phase is found by varying the lattice constants of the supercell followed by a conjugate gradient relaxation of all atoms in the cell. The same lattice relaxation with a fixed cell geometry is done for the structures under hydrostatic pressure.

The structure of the various possible phases of Si_2CN_4 are shown in Fig. 1. The β structure is hexagonal with a $P6_3/m$ space group[16] and here we have considered various modifications of the β-Si_3N_4 structure with a C atom replacing Si and vice versa. Two possible locations have been considered for the C atoms in the β structure, corresponding to whether C is located on adjacent nearest neighbor anion sites or second neighbor anion sites. We denote the former modification as β^* and the latter as the β structure. As we shall see the β^* structure is slightly metastable relative to the β structure implying that the C-N-C bond structure is not preferred. However the largest angle along the N-C-N bond structure in the β^* is bigger than in the β phase and, as we shall argue, the metastable β^* phase could lead to the spinel structure under compression whereas the β phase may not.

More recently a spinel structure with $Fd3m$ symmetry has been synthesized for both Si_3N_4 (Ref. 17) and Ge_3N_4.[7] As with the β structures we consider modifications of this
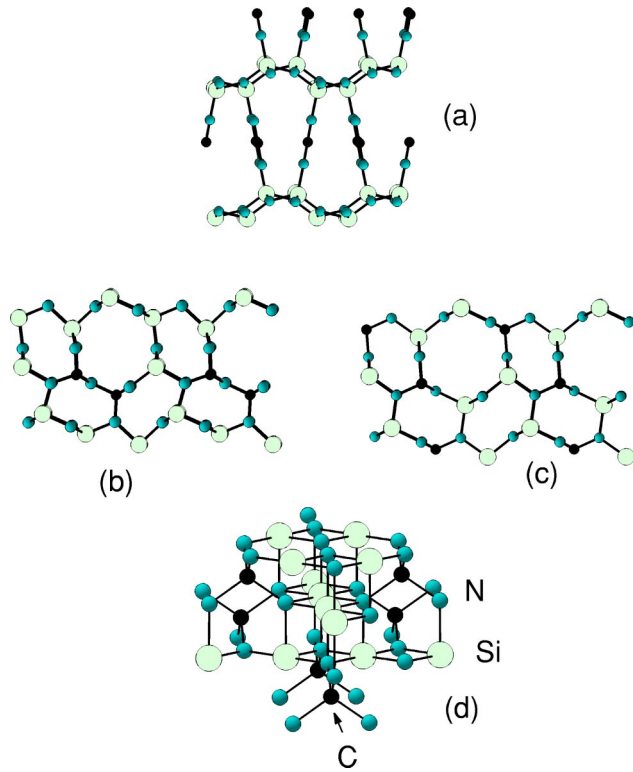
FIG. 1. The precursor $Aba2$ phase (a), metastable β^* phase with two types of N-C-N bonds (b), conventional beta phase with only one type of N-C-N bonds (c), and the spinel phase (d) of Si_2CN_4.

FIG. 2. Charge densities of β-Si_2CN_4. Contours are in units of $me/(bohr^3)$.

TABLE I. Calculated properties of Si_2CN_4.

phase	Z	lattice (Å)	B(GPa)	$\rho(g/cm^3)$
$Aba2$	4	$a = 5.45^a$, 5.35^b, (5.44^c)	168	2.3^a
		$b = 13.81^a$, 13.65^b, (13.58^c)	79 ± 10^b	2.3^b
		$c = 4.82^a$, 4.92^b, (4.81^c)		
		C:(0.0000,0.0000,0.0000)		
		Si:(0.0987,0.2032,0.9538)		
		N:(0.8728,0.2698,0.1097)		
		N:(0.0389,0.0851,0.0045)		
β	2	$a = b = 7.25$; $c = 2.72$	283 (287^d)	
$(P2/m)$		Si:(-0.7832,-0.5943)		
		Si:(0.1619,0.7570)		
		C:(0.548 67,-0.188 80)		
		N:(0.3423,0.0549)		
		N:(-0.3169,0.0027)		
		N:(0.3327,0.0275)		
		N:(0.3578,0.6785)		
Spinel	8	$a = 7.32$ (7.29^e)	344 (309^e)	
$(Fd3m)$		$u = 0.3736$ (0.3885^e)		

[a]From Ref. 4.
[b]From the SCC-DFTB calculations.
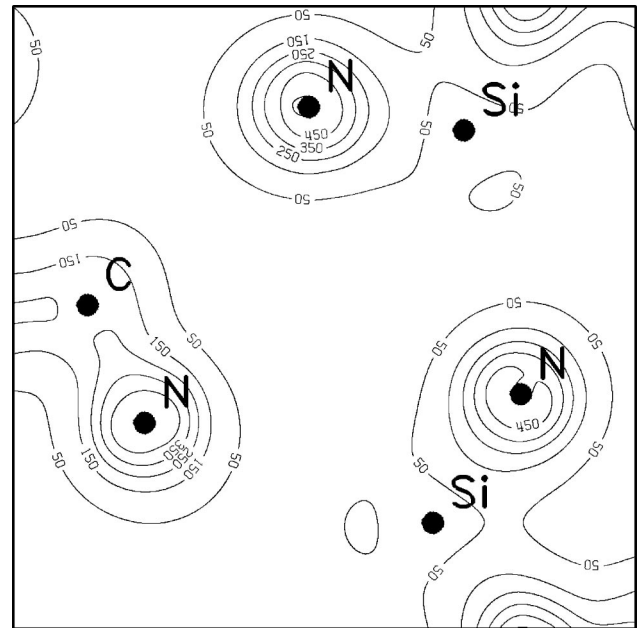[c]Experimental value from Refs. 3,15.
[d]From Ref. 15.
[e]From Ref. 16.

spinel structure with C atoms replacing Si. The C atom was placed on a site in the spinel lattice where it has tetrahedral symmetry. As shown recently[3] when C occupies the tetrahedral site of the spinel structure, the bulk modulus has the largest value. Details of the calculated structures are given in Table I.

In Figs. 2 and 3 we present electronic charge densities of the β and $Aba2$ structures, respectively. These charge densities are shown in planes of the appropriate structures to highlight the relative importance of the Si-N and C-N bonds. It is quite clear that in both structures the C-N bond is far
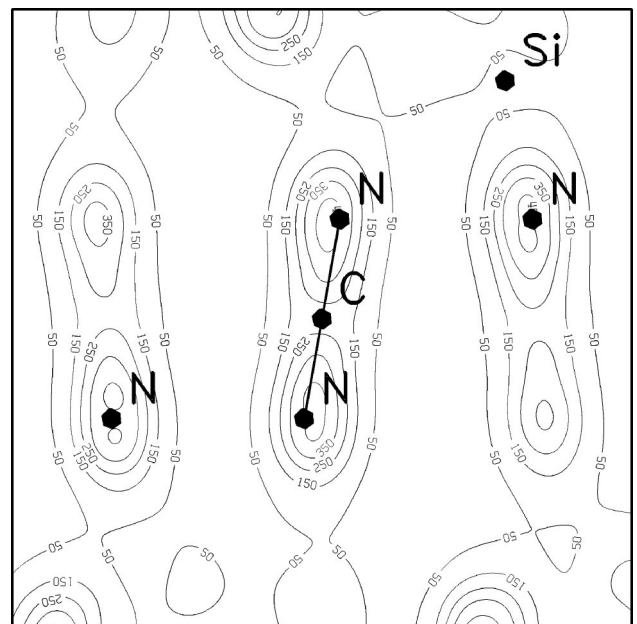
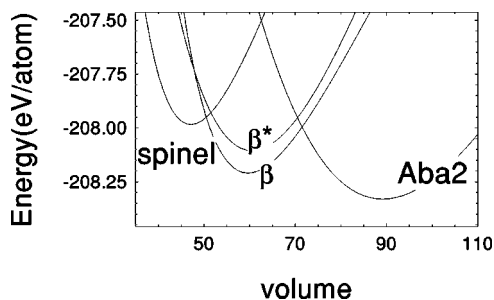

FIG. 3. Charge densities of the $Aba2$ phase of Si_2CN_4.

FIG. 4. Energy-volume(bohr^3) equation of state of Si_2CN_4 using parameters given in Table I.

FIG. 6. Angular variation of the interplanar N-C-N bond of the $Aba2$ phase of Si_2CN_4 under isotropic compression as calculated by plane wave and the SCC-DFTB methods. The N-C-N bond in β phase is $\sim 150°$, in the β^* phase it is $\sim 160°$, and in the spinel phase it is 178°. A relative volume compression of 0.90 corresponds to a calculated pressure of about 20 GPa. Only the average value of the bond angles is shown once collapse has occurred.

more covalent than Si-N bonds. The importance of C in affecting the bonding in these structure is also consistent with recent results[18] on a series of spinel related structures where the inclusion of C is associated with the larger bulk moduli.

Most important in relation to material synthesis are the transition pressures needed to transform from one physical state to the next. The calculated energies and pressures—as deduced from the slope of the energy-volume equation of Birch equation of state[12]—is shown in Fig. 4.

It is quite clear from the results of Figs. 4 and 5 that an extensive volume compression is needed for the $Aba2$ phase to coexist with either the β or the spinel structures. But there could be other difficulties in the fundamental geometrical structure of this phase and how it can relate to the high pressure superhard phases. Kroll *et al.*[4] suggested that the rigidity of the Si-N-C-N-Si bond that essentially connects Si-N layers in the $Aba2$ structure is a major obstacle to be overcome if this structure is to be used as a precursor phase for ultrahard structures. At zero pressure and temperature, the calculated angle between the N-C-N interplanar linkages is 177.8° for the *ab initio* calculation with a fundamental unit cell of 28 atoms and 169.3° for the SCC-DFTB approach with 252 atoms. This slight difference of less than 5% is due to the different approaches. We have followed the behavior of this bond under extreme uniform compression and Fig. 6 shows how this angle varies as such. Likewise in Fig. 7 we
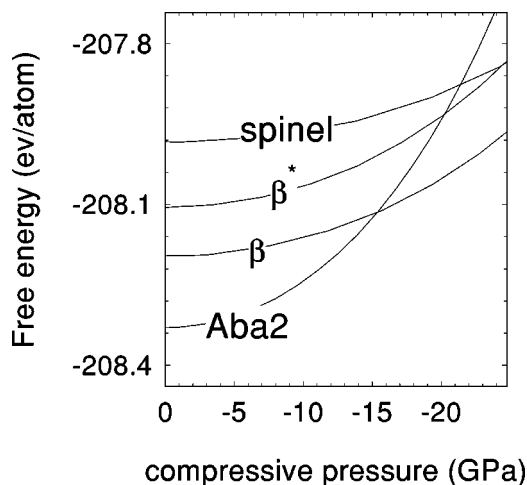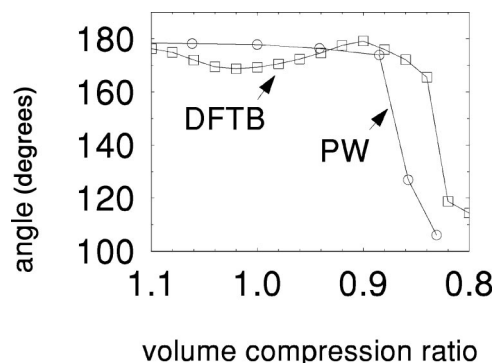
show the variation of bond length for each of the C-N and Si-N bond lengths. During the uniform compression, the N-C-N bond angle and the C-N and Si-N bond lengths only change slightly regarding the results of both theoretical methods, but the strong, almost linear N-C-N chain tilts more and more. The abrupt collapse of this bond when essentially the $Aba2$ phase displays significant disorder is clearly demonstrated.

Before we discuss this behavior we first consider similar bonds in the β and spinel phases. In the lowest energy β phase the C atoms lie in nontetrahedral but fourfold coordination with N with a maximum angle between the N-C-N bonds of $\sim 150°$. Si atoms interconnect these structures. On
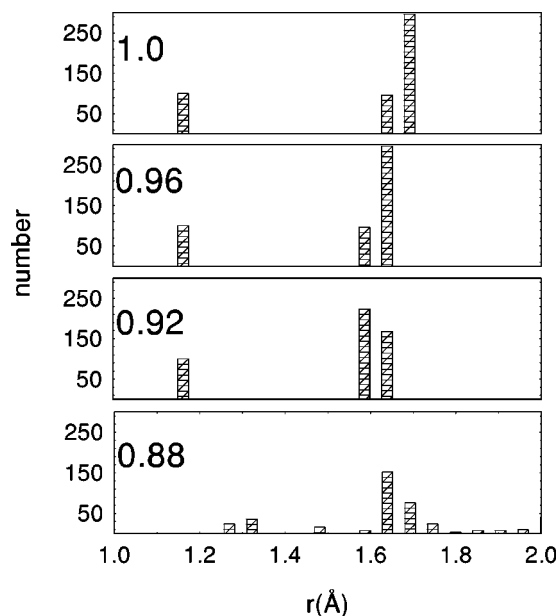

FIG. 5. Free energy-pressure equation of state of Si_2CN_4. Negative pressure is compressive pressure.

FIG. 7. Radial distance distribution of the $Aba2$ phase of Si_2CN_4 under isotropic compression—the volume ratio is indicated. The lowest value is the C-N bond length, the higher value for the Si-N bond length.

the contrary in the relatively metastable β^* structure, in addition to the fourfold coordinated structures are near linear N-C-N structures. In this case the angle between the N-C-N bonds is somewhat larger being $\sim 160°$. If we examine Fig. 6 which shows calculated volume compression of the Si-N-C-N-Si bond angles in the $Aba2$ phase then we clearly see that this bond is unlikely to reach either of these values unless significant compression is achieved. We do note that the bond could attain the larger value of $\sim 160°$ evident in the β^* structure before the lower one of the more stable β structure.

It is quite difficult to be precise about the pressure that will cause the bond to collapse, yet some estimate can be obtained from the relative energy difference of the $Aba2$ phase at a relative volume compression of about 0.90—we estimate that the bond collapses below this volume compression. The energy-volume equation of state indicates that at such a compression there is an energy change of ~ 0.2 eV/atom and, in turn, this corresponds to a pressure of around 20 GPa. From the free energy results this is in excess of the ~ 16 GPa at which both the β and $Aba2$ phases can coexist and thus we argue that the β phase can be synthe-

sized from the $Aba2$ phase only above a pressure of ~ 20 GPa—when the bonds collapse. The transition therefore would need some additional kinetic mechanism.

At the same time we note the synthesis path also predicted from the calculated equation of state for each phase. At a pressure of ~ 20 GPa the transition $Aba2 \rightarrow \beta$ is permitted as we have discussed. Yet once the β phase is attained, incompressibility of this phase cannot lead to the spinel structure as the Free energy-volume equations of state do not intersect at any reasonable pressure. In other words, formation of the β phase would block any subsequent formation of the spinel phase.

In conclusion we have investigated the relative energetics of some possible phases of Si_2CN_4 deducing their elastic properties and possible transitions pressures. A major hindrance with the $Aba2$ precursor phase is the very strong N-C-N bond—yet we predict this near-linear bond will collapse under significant compression at pressures above 20 GPa and this could possibly lead to ultra hard structures. The first such structure is a β phase, yet should such a structure emerge this will prevent formation of the spinel phase.

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