

ARTICLES

Structural stability of some possible phases of SiC_2N_4

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The potentially superhard material $\beta\text{-SiC}_2\text{N}_4$ is compared with $\beta\text{-C}_3\text{N}_4$ where electron density considerations suggest that the strength of the materials relates to the C-N bond. A recently postulated cubic phase has been modeled and related to the β phase. The structure may be a promising precursor to a superhard β phase if the necessary concentration of N can be realized. [S0163-1829(99)06041-5]

I. INTRODUCTION

The β form of Si_3N_4 was the prototype material leading to the postulate that C_3N_4 may be harder than diamond.^{1,2} It is softer than $\beta\text{-C}_3\text{N}_4$ with a measured bulk modulus of 256 GPa,³ as compared to the theoretically predicted value for $\beta\text{-C}_3\text{N}_4$ of 437 GPa.⁴ Recently tertiary ceramics in the form Si-C-N are being investigated⁵⁻⁸ for potentially superhard properties. Amorphous forms of Si-C-N materials are well documented⁹ but often such materials are reported to segregate into SiC or Si_3N_4 when heated; a stable crystalline form of Si-C-N that does not behave in such a manner is being sought. Crystalline Si-C-N compounds that have so far been produced have had their structure contested depending upon the nature of the locality about Si. Using extended x-ray-absorption fine-structure studies (EXAFS) either a local tetrahedral¹⁰ or random¹¹ structure about Si has been suggested. In both these cases Si atoms are linked by a C-N network. More recent EXAFS measurements⁸ coupled with computer modeling favored the local tetrahedral Si-N-C arrangement. The crystalline structure of this Si-C-N material was found to have a structure very near to that of $\alpha\text{-Si}_3\text{N}_4(P3_1c)$ with a unit cell of dimension $a = 6.904 \text{ \AA}$ and $c = 5.260 \text{ \AA}$.

The importance of the local tetrahedral structure has also been noted in the analysis of a lower density form of SiC_2N_4 compound recently produced by Riedel and co-workers.⁶ Here x-ray diffraction showed the possibility of an apparent cubic ($Pn3m$) phase with a cubic unit cell of measured dimension $a = 6.1885 \text{ \AA}$. In such a material the local Si related tetrahedral structure is realized as SiN_4 units that are connected through N-C-N chains. The flexibility of the N-C-N bond has been considered an essential feature for more extended SiC_2N_4 structures.^{6,12}

Following earlier theoretical results on $\beta\text{-C}_3\text{N}_4$, one of the hardest forms of SiC_2N_4 is expected to be $\beta\text{-SiC}_2\text{N}_4$. This is obtained by replacing two C atoms in the 14 atom unit cell of $\beta\text{-C}_3\text{N}_4$ with Si atoms maintaining the lowest C-N bond lengths. Possibly this form can be attained through a synthesis starting from one of structures discussed above. The purpose of this paper, therefore, is to consider details of the structures and to relate these to the potentially superhard

form of the material $\beta\text{-SiC}_2\text{N}_4$.

II. COMPUTATIONAL DETAILS

Soft Troullier-Martins¹³ non-spin-polarized pseudopotentials with plane waves of 64 Ry were used throughout with a k -point sampling using a [444] Monkhorst-Pack grid.¹⁴ Energy-volume relations were calculated using a plane-wave algorithm¹⁵ for each structure and the results fitted to a standard equation of state¹⁶ from which an estimate of the bulk modulus can be obtained. Each structure was optimized for a specified cell geometry with lattice relaxation included in each case. This procedure is proving to be quite reliable in the computational design of advanced materials.

A. $\beta\text{-C}_3\text{N}_4$ and $\beta\text{-SiC}_2\text{N}_4$

In Fig. 1 we show the structure of $\beta\text{-SiC}_2\text{N}_4$ as viewed along the c axis of the hexagonal unit cell. The starting structure for $\beta\text{-SiC}_2\text{N}_4$ was $\beta\text{-C}_3\text{N}_4$ but with relaxation the Si atoms moved yielding an overall symmetry of $P2/m$ as opposed to $P6_3/m$ as for $\beta\text{-C}_3\text{N}_4$. The $P2/m$ structure is identical to $P6_3/m$ when the magnitude of the unit-cell vectors \mathbf{a} and \mathbf{b} is the same and the angle between \mathbf{a} and \mathbf{b} is 120° , held fixed here. Our results are given in Table I.

The relaxation of atoms in both structures is such that the lowest C-N bond length is 1.45 \AA and the bulk modulus of SiC_2N_4 is about $\frac{2}{3}$ of C_3N_4 . This result agrees with previous calculations¹⁷ and implies that the origin of the bulk modulus relates to the strong C-N bond. This is confirmed by further

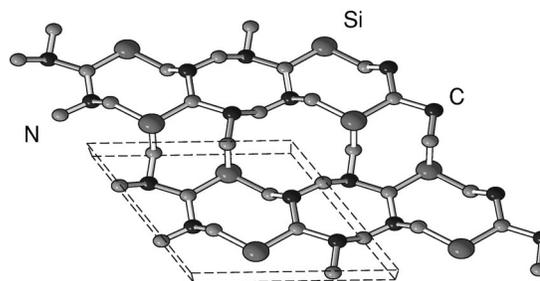
FIG. 1. β phase of SiC_2N_4 .

TABLE I. Calculated properties of β - C_3N_4 and β - SiC_2N_4 . Spin-polarization correction energies of $-0.78(\text{Si})$, $-1.4(\text{C})$, and $-2.92(\text{N})$ have been used when calculating the binding energies.

Material	Unit cell (\AA)	Fractional coordinates	B (GPa)	B'	Binding energy (eV)
β - C_3N_4 ($P6_3/m$)	$a = b = 6.41$	C:(0.1780,0.7720,0.2500)	432	3.95	-6.673
	$c = 2.40$	N:(0.3310,0.0330,0.2500)			
		N:(0.3333,0.6667,0.2500)			
β - SiC_2N_4 ($P2/m$)	$a = 6.78$	Si:(0.6038, -0.1709, 0.2500)	330	4.01	-6.601
	$b = 6.92$	C:(0.1661, 0.7550, 0.2500)			
	$c = 2.58$	C:(-0.7883, -0.5853, 0.2500)			
		N:(0.3101, -0.0049, 0.2500)			
		N:(-0.2821, -0.3445, 0.2500)			
		N:(-0.0299, 0.3080, 0.2500)			
		N:(0.3130, 0.6572, 0.2500)			

calculations on β - Si_2CN_4 and β - Si_3N_4 ,¹⁷ where a steady reduction in the bulk modulus is found.

In Figs. 2 and 3 we show the calculated charge density in one of the hexagonal planes. There are two important features to be noted on comparing these figures. First, very little charge is located about the Si atom—again suggesting that Si bonding is insignificant compared with the C-N bond. Second is the direction of the C-N bonding; if we look at the N atom we see that the main charge is *not* directed along the C-N bond itself but with N($2p$) orbitals being directed perpendicular to the bond. Surprisingly the C-N bond is very similar in both silicon-carbon-nitride and carbon nitride again suggesting the importance of the C-N bond.

B. Near-cubic forms of SiC_2N_4

Recently a low-density phase of SiC_2N_4 has been investigated⁶ with a possible cubic structure ($Pn3m$) shown in Fig. 4(a). In such a structure, Si surrounded tetrahedrally

by four N atoms is the essential building block and a linear Si-N-C-N-Si bridging unit. The measured unit-cell constant is 6.18 \AA , and Riedel *et al.* noted that this size of cell would have a short interatomic spacing between the C and N atoms of 1.19 \AA . They, therefore, suggested that the measured cell constant may correspond to an effective value relating to a random distribution of N atoms about the Si-C-Si unit. The linearity of the N-C-N bond can also be maintained in a similar symmetry in the manner suggested in Fig. 4(b) and more recently Kroll *et al.*¹² have suggested another structure for the cubic phase involving the N-C-N bond with overall $P\bar{4}n2$ symmetry shown in Fig. 4(c). The nonlinear C-N-C bond is expected to lead to a softening of the structure.¹⁸ As yet the several cubic structures have not been related to the potentially super-hard β - SiC_2N_4 phase. We have calculated the structure of the three possible phases and the results are given in Table II. Each of the structures has a rather low bulk modulus suggesting a low compressibility and, for that matter, possibly a low resistance to shear deformation in view of the almost linear bond directionality.

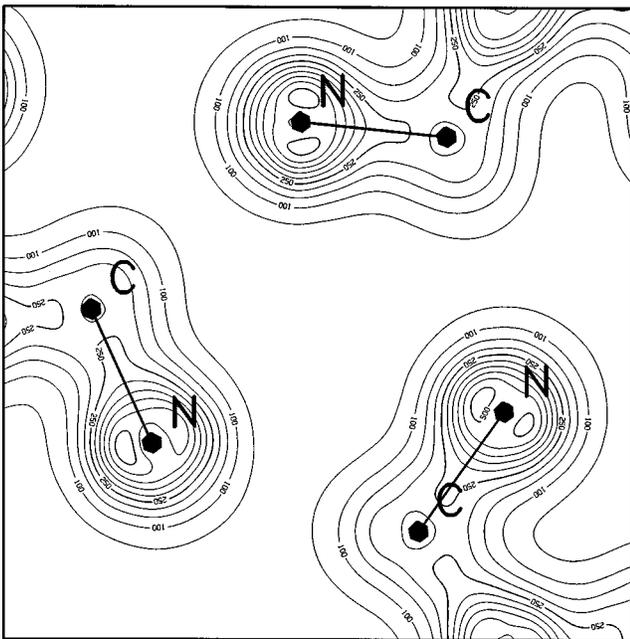


FIG. 2. Charge density (in units of me/bohr^3) of β - C_3N_4 plotted perpendicular to the c axis.

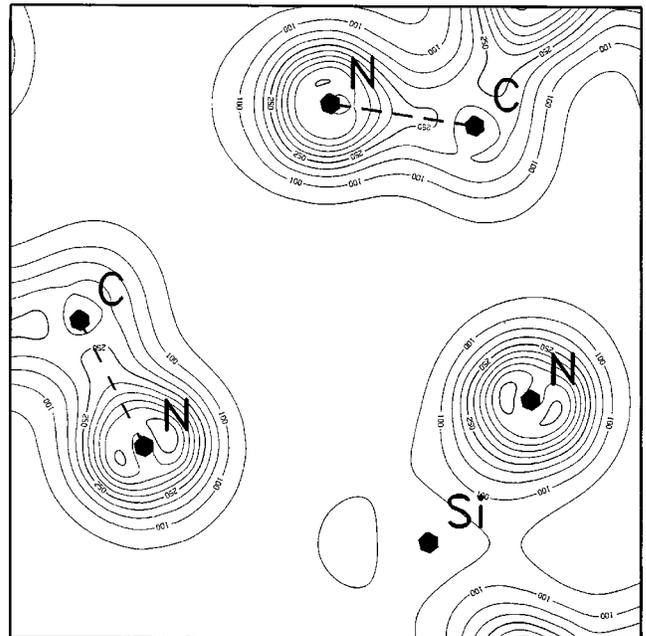


FIG. 3. Charge density β - SiC_2N_4 .

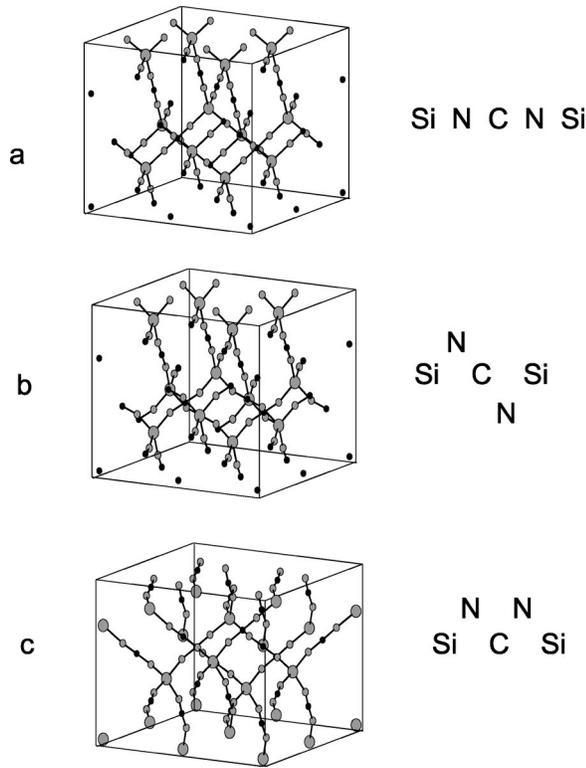


FIG. 4. Cubic phase of SiC_2N_4 . Large open circles are Si, small black circles C and small open circles N. The directional nature of the Si-N-C-N-Si bond is shown for each case.

As with the β structure discussed earlier, it is interesting to examine the charge density especially along the Si-N-C-N-Si bond. In the exact cubic structure labeled a in Fig. 4 this is shown in Fig. 5. Unlike the β phase, the bond is quite directional.

C. Transition to the β phase

In Fig. 6 we show the energy-volume relations for each model of the cubic phase and for the β - SiC_2N_4 phase. The energy of each of the cubic phases lies *below* that of the β phase. This is not unlike the situation for graphite and diamond and so a cubic to β -phase synthesis may be possible. In Fig. 7 we show the related energy-pressure relation as obtained from the equation of state; the pressures needed to transform each of the cubic phases to the β phase lie in the range 6–12 GPa.

Another way of estimating the transition pressure needed to change from one phase to another is from the slope at the energy intersection of the common phases—this is the pres-

TABLE II. Calculated properties of some possible *cubic* phases of SiC_2N_4 . Phase *b* is a defective form of phase *a* used to model the bonding indicated in Fig. 4(b). The experimentally observed lattice parameter is $a = 6.18 \text{ \AA}$ (Ref. 6).

Phase	a (\AA)	B (GPa)	B'	Binding energy (eV)
<i>a</i> ($Pn3m$)	6.64	106	3.90	-6.649
<i>b</i>	6.65	95	2.68	-6.630
<i>c</i> ($P\bar{4}n2$)	6.32	32	4.89	-6.653

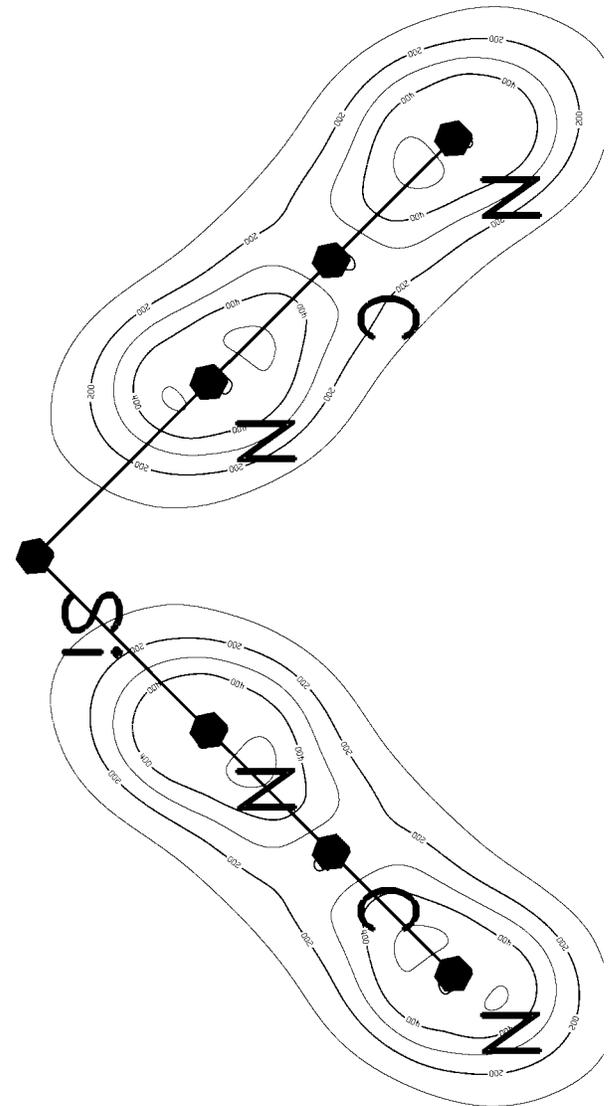


FIG. 5. Charge density of the $Pn3m$ phase a of cubic SiC_2N_4 .

sure necessary to overcome the energy barrier between the two phases. In the softer of the three cubic phases the pressure is quite large—about 62 GPa. However, if we simulate the transformation from graphite into diamond in a similar

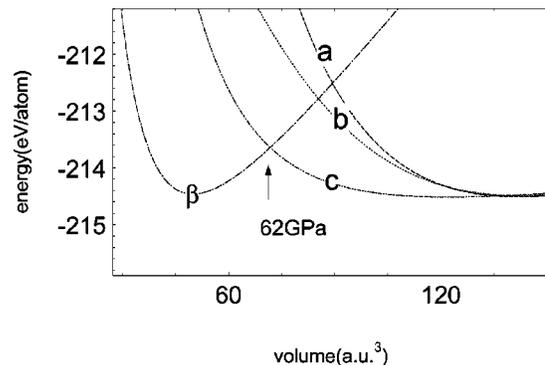


FIG. 6. Energy-volume behavior of different phases of SiC_2N_4 . *a*, *b*, and *c* label the different phases shown in Fig. 4. The pressure shown is obtained from the intersection point of the *c* phase and the β phase.

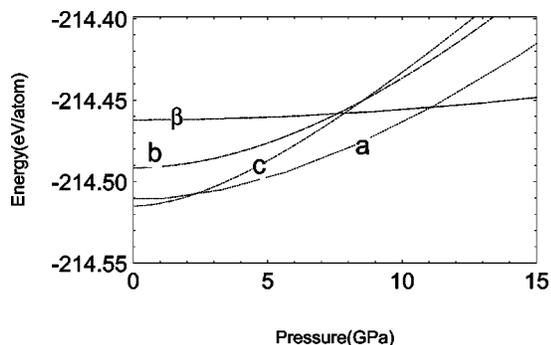


FIG. 7. Energy pressure for different phases of SiC_2N_4 . *a*, *b*, and *c* label the different phases shown in Fig. 4.

way we calculate a pressure of $P=80$ GPa is needed to transform graphite into diamond by overcoming the energy barrier. A commercial synthesis process involves pressures far less than this. The transformation process of graphite into diamond itself is not continuous but involves changes from graphite into other (rhombohedral) graphitic forms through to hexagonal diamond and finally diamond. In addition, chemical influences (such as a metal flux) and temperature factors are important in the synthesis. Collectively these latter features are influencing the relative energetics of the various phases. Thus we must conclude in a conversion from the cubic form of SiC_2N_4 to the β phase that the lower calculated value of between 6–12 GPa would signify some lower limit on the required pressure provided another route can be used to overcome the energy barrier separating the phases. The upper limit of pressure, namely 62 GPa, is the pressure without other factors.

III. DISCUSSION

We have established that the origin of any potential hardness in a tertiary material like $\beta\text{-SiC}_2\text{N}_4$ relates to the C-N bond that is in appearance very similar to that in $\beta\text{-C}_3\text{N}_4$. In view of the potential hardness of $\beta\text{-SiC}_2\text{N}_4$, and the recent discovery of relatively low-density phases, routes through which the material can be synthesized merit investigation. For each of the cubic structures we have investigated there is not agreement with experiment. Two of the structures with a linear N-C-N bond have cell constants far larger than the observed value. A nonlinear N-C-N bond does give a lower cell constant yet still this is larger than the observed value. We do not think that the reason for the disagreement is due to the computational model or if another structure is applicable. Rather we would concur with the speculation⁶ that a random or nonstoichiometric distribution of N is responsible for the observed lattice constant. This would not be unlikely as it is well known that it is difficult to get large amounts of N to interact with C. Further work, both experimental and theoretical, is needed to resolve this issue, yet if indeed the needed amounts of N can be accommodated to create some potential cubic structures that have been investigated here then such structures hold promise for a synthesis of the potentially superhard $\beta\text{-SiC}_2\text{N}_4$.

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