

Is carbon nitride harder than diamond? No, but its girth increases when stretched (negative Poisson ratio)

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Abstract

It has been believed that C_3N_4 ceramic would be harder than diamond. Predictions are reported of the mechanical properties based on a force field derived from ab initio quantum mechanics. The predicted structure for α - C_3N_4 is in good agreement with transmission electron diffraction (TED) studies, supporting the identity of the films as α - C_3N_4 . The bulk modulus of α - C_3N_4 is calculated to be 189 GPa, significantly less than diamond (436 GPa calculated, 442 GPa experimental). However, α - C_3N_4 is predicted to have a negative Poisson ratio. This may lead to interesting applications.

1. Introduction

A great deal of interest was sparked by a recent prediction [1,2] that carbon nitride (β - C_3N_4 , with the same structure as β - Si_3N_4) is even harder than diamond. A number of groups have attempted [3–7] to form thin films of C_3N_4 , and two [3,7] claim to have successfully synthesized β - C_3N_4 thin films.

The previous predictions [1,2] were state-of-the-art first principle calculations (local density approximation (LDA)), however several significant assumptions were made that could affect the results. Thus, structures with nonplanar N atom were not considered (in analogy to Si_3N_4 which has planar N). In addition, to obtain the compressibility each coordinate was assumed to scale uniformly.

2. The force field (MSFF) for C_3N_4

To obtain a force field suitable for predicting mechanical properties, we carried out ab initio calculations [8,9] (Hartree–Fock (HF) wavefunctions, 6-31G** basis) on cluster models. Thus for diamond we used adamantane [10,11] ($(CH)_4(CH_2)_6$ a cubic molecule), and for C_3N_4 we used the analogous hexamethylenetetramine (HMT [12,13], $N_4(CH_2)_6$).

The force field involves two types of terms [14]:
(i) Bond stretch (Morse potential), $E_{\text{bond}} = D\{\exp[-\alpha(R - R_e)] - 1\}^2$, where R is the bond length, R_e and D are the equilibrium position and depth of the well, and $k_R = 2D\alpha^2$ is the stretching force constant. (D was not adjusted (standard bond energies were used).)

(ii) Angle-bend (harmonic potential), $E_{\text{angle}} = \frac{1}{2}k_\theta(\theta - \theta_e)^2$, where θ is the bond angle, θ_e is the equilibrium angle, and k_θ is bending force constant.

We used the two totally symmetric (A_1) distortions of the nonhydrogen framework of these clusters

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Table 1

Predicted properties of C_3N_4 and diamond crystals using the MSFF. Density (ρ), lattice parameters (a, c), bulk modulus (B), and energy (E) are reported

		ρ (g/cc)	a (Å)	c (Å)	B (GPa)	E^a (kcal/mol)
optimized structure						
α - C_3N_4	present work	3.78	6.35	4.64	189	0.0
β - C_3N_4	present work	3.56	6.35	2.46	250	25.1
planar nitrogen						
α - C_3N_4	present work	3.45	6.59	4.71	351	54.0
β - C_3N_4	present work	3.50	6.38	2.47	357	29.5
β - C_3N_4 (scaled)	present work				366 ^b	
β - C_3N_4 (scaled)	LDA ^c		6.44		427	–
diamond						
	present work	3.566	3.550	3.550	436	–
	LDA ^c	3.573	3.548	3.548	444	–
	exp. ^d	3.516	3.567	3.567	442	–

^a Per formula unit C_3N_4 .

^b B was calculated assuming uniform scaling all of atom coordinates.

^c See Refs. [1,2]. ^d See Ref. [23].

to determine the parameters. The results are: Morse C–N and C–C bond stretches ($R_e = 1.460$ and 1.537 , $k_R = 898(808)$ and $743(669)$, $D = 73$ and 83 for $N_4(CH_2)_6$ and $(CH)_4(CH_2)_6$, respectively), CNC and CC_1C angle bends ($\theta_e = 108.273$ and 109.353 , $k_\theta = 284(227)$ and $233(186)$ for $N_4(CH_2)_6$ and $(CH)_4(CH_2)_6$, respectively), and NCN and CC_sC angle bends ($\theta_e = 111.820$ and 109.708 , $k_\theta = 233(186)$ and $233(186)$, respectively). Pulay and Meyer [15–17] showed that to obtain experimental vibrational frequencies, the HF force constants must be scaled by 0.9 for bond stretch and 0.8 for angle bend leading to the values given in parentheses. These scaled parameters are used in the molecular simulation force field (MSFF). We developed similar force fields involving the hydrogen atoms, and then applied these force fields to adamantane and HMT molecules. The calculated and experimental [18–20] frequencies match within a few percent for the framework A_1 vibrational modes of the $(CH)_4(CH_2)_6$ and $N_4(CH_2)_6$ molecules (749 versus 757 cm^{-1} for $1A_1$ and 1015 versus 970 cm^{-1} for $2A_1$ in $(CH)_4(CH_2)_6$; and 812 versus 782 cm^{-1} for $1A_1$ and 1030 versus 1041 cm^{-1} for $2A_1$ in $N_4(CH_2)_6$).

The inversion or umbrella motion at the N is expected to be quite different for C_3N_4 than for Si_3N_4 crystal. The reason is that $N(SiH_3)_3$ is planar [21] whereas $N(CH_3)_3$ is pyramidal [22]. From ab initio methods (HF, 6-31G** basis), we calculate

that $N(CH_3)_3$ has $\theta_{CNC} = 111.9^\circ$ (the experimental value is 110.9°) [22] with an energy barrier of value 7.9 kcal/mol for inversion (the experimental value

Table 2

Calculated powder-diffraction pattern for α - C_3N_4 , β - C_3N_4 compared with TED experiments^a

TED ^a		α - C_3N_4		β - C_3N_4	
d (Å)	intensity	d (Å)	hkl	d (Å)	hkl
		5.50	100 m	5.50	100 m
3.43	w	3.55	101 s		
3.15	m	3.17	110 s	3.17	110 m
2.65	vw	2.75	200 m	2.75	200 s
		2.37	201 s		
2.18	s	2.14	102 s	2.25	101 s
2.07	s	2.08	210 m	2.08	210 s
1.92	w	1.87	112 s	1.95	111 m
		1.90	211 m	1.83	300 m
1.76	w	1.77	202 w		
1.64	w	1.70	301 m		
1.56	vw	1.49	103 vw	1.59	211 w
		1.45	311 vw	1.52	310 w
				1.47	301 w
				1.33	221 w
1.25	s	1.31	222 m	1.26	320 vw
1.17	vw	1.22	321 m	1.23	002 w
		1.16	004 vw		
1.11	vw	1.11	322 w	1.12	321 m
		1.09	114 w		
1.07	m	1.07	412 m	1.08	411 w
		1.06	330 w		

^a Ref. [7].

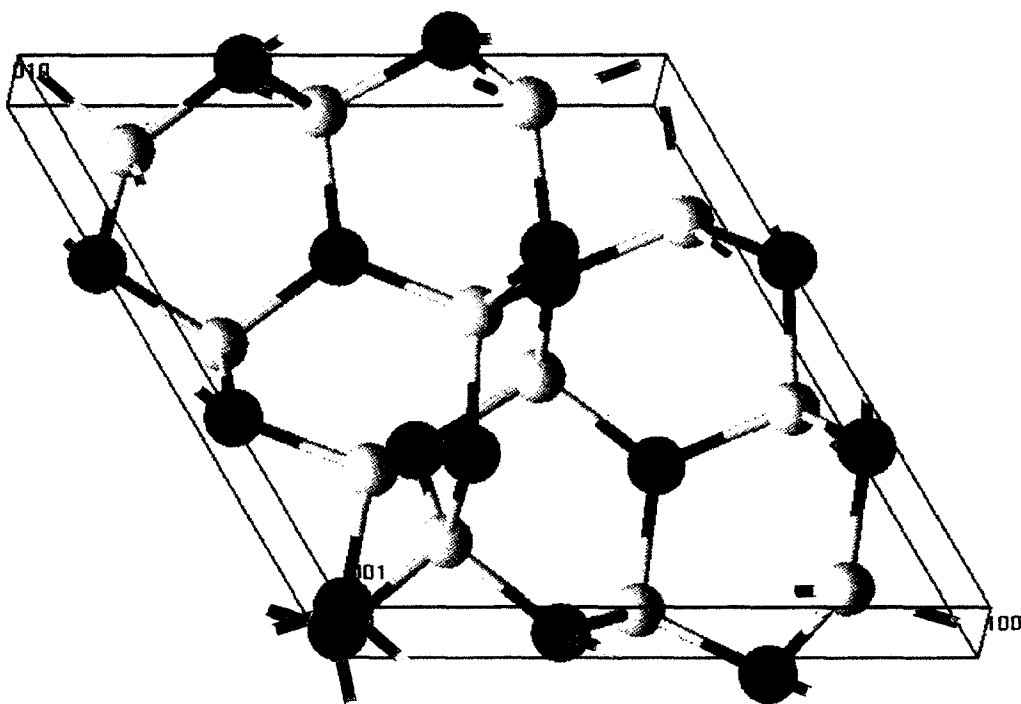


Fig. 1. The predicted crystal structure for α - C_3N_4 .

is 8.1 kcal/mol, and the MSFF predicts of 8.6 kcal/mol). In contrast, for $N(\text{SiH}_3)_3$ we calculate $\theta_{\text{SiNSi}} = 120^\circ$ (planar) in agreement with experiment [21] (it costs an energy of 6.9 kcal/mol to bend the angles to 111.9°). Thus replacing Si in Si_3N_4 with C leads to a 15 kcal/mol additional driving force for pyramidal structures.

3. Structure of C_3N_4 crystals

The MSFF leads to the crystalline properties² in Table 1. For diamond we predict a lattice constant too small by 0.46% and a bulk modulus too low by 1.8%. This suggests that the MSFF leads to reliable structural and mechanical properties.

² All calculations of structure and properties of crystal phases were carried out with POLYGRAF from Molecular Simulation Inc. (Burlington, Massachusetts). Cerius² from MSI was used to calculate the TED data.

Using the MSFF we calculated the structural parameters for α - C_3N_4 and β - C_3N_4 (with topologies corresponding to α - Si_3N_4 and β - Si_3N_4), fully optimizing all atomic and cell parameters (see footnote 2). The space group for α - C_3N_4 is calculated to be P31c (C_{3v}^4) with four formula units per unit cell ($a = 6.35$ and $c = 4.64 \text{ \AA}$)³. It has spheroidal cavities (diameters of 4.1–5.2 \AA) into which pyramidal nitrogens protrude. The optimum structure for β - C_3N_4 is calculated to have the P3 (C_3^1) space group with two formula units per unit cell ($a = 6.35$, $c = 2.46 \text{ \AA}$)⁴ (β - Si_3N_4 has higher symmetry $P6_3/m$ due to the planar N atoms). It has cylindrical cavities

³ The fraction coordinates of α - C_3N_4 are C1 (0.0707, 0.5063, 0.6817), C2 (0.2525, 0.1688, 0.4754), N1 (0, 0, 0.5359), N2 ($\frac{1}{3}$, $\frac{2}{3}$, 0.6615), N3 (0.6564, 0.6490, 0.4254), and N4 (0.3537, 0.3025, 0.7402).

⁴ The fractional coordinates of β - C_3N_4 are C1 (0.7805, 0.1803, $\frac{1}{4}$), C2 (0.2301, 0.8250, $\frac{3}{4}$), N1 ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}$), N2 ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{3}{4}$), N3 (0.0354, 0.3624, $\frac{1}{4}$), and N4 (0.9610, 0.6907, $\frac{3}{4}$).

(diameters of 3.6 to 4.4 Å) into which nitrogens protrude.

We find that α - C_3N_4 is far more stable than β . This is because the N in C_3N_4 strongly prefers to be nonplanar whereas the N in β - Si_3N_4 strongly prefers to be planar. The β structure forces some N to be planar, making it 3.4 kcal/mol more stable than α for Si_3N_4 (for Si_3N_4 only a transformation from α to β has been observed, never the reverse [24]). The preference of N to be pyramidal when bonded to C stabilizes α - C_3N_4 by 25 kcal/mol = 105 kJ/mol per formula unit. (The β structure forces half the N to be planar, accounting for ≈ 16 kcal/mol of the difference). This large energy difference suggests that only α - C_3N_4 would be formed with thin film techniques.

Two recent experiments on the C–N films [3,7] have been interpreted in terms of the β - C_3N_4 structure (assuming planar N), and one reported transmission electron diffraction (TED) data (indexed for β - C_3N_4) [7]. Table 2 shows the powder-diffraction pattern we calculated (see footnote 2) for the predicted structures of α - C_3N_4 and β - C_3N_4 and compares with the TED data [7]. Thus we conclude that the thin film in Ref. [7] is indeed α - C_3N_4 .

4. Properties of C_3N_4 crystals

The predicted bulk modulus of α - C_3N_4 is just 43% of the value for diamond (189 versus 436 GPa), indicating that C_3N_4 is much softer than diamond.

Why did the earlier theory [1,2] obtain different results? They were state-of-the-art first principle calculations (local density approximation (LDA)) and remain so; however, due to the large unit cell it was necessary to make some simplifications. In particular, structures with *nonplanar* N were *not considered* (in analogy to Si_3N_4 which has planar N). We find that this restriction nearly doubles the bulk modulus to 357 GPa, which is just 18% less than diamond. A second constraint in the early calculations is that each coordinate was assumed to scale uniformly. This further increases the bulk modulus to 366 GPa (16% less than diamond).

Although not unusually hard, α - C_3N_4 does possess a remarkable property. It has a *negative* Poisson ratio (Table 3). Normally, stretching a solid in one

Table 3

Calculated mechanical properties (see footnote 2 in the text) of α - C_3N_4 , β - C_3N_4 and diamond

	α - C_3N_4	β - C_3N_4	Diamond calc. (exp.)
elastic constants (GPa)			
$C_{11} = C_{22}$	576.0	550.9	1052.5 (1077.0)
C_{33}	700.3	922.1	1052.5 (1077.0)
C_{12}	-31.3	196.5	128.4 (124.7)
$C_{13} = C_{23}$	-16.8	-38.2	128.4 (124.7)
$C_{15} = -C_{25}$	-19.8	0.0	0.0 (0.0)
$C_{44} = C_{55}$	279.0	263.8	476.1 (577.0)
C_{66}	303.6	177.0	476.1 (577.0)
C_{46}	19.8	0.0	0.0 (0.0)
young modulus (GPa) and Poisson ratios			
$E_x = E_y$	572.6	480.1	1024.5 (1051.1)
μ_y	-0.0527	0.3550	0.1087 (0.1038)
μ_z	-0.0252	-0.0266	0.1087 (0.1038)
E_z	699.2	918.1	1024.5 (1051.1)
$\mu_x = \mu_y$	-0.0308	-0.0509	0.1087 (0.1038)
bulk modulus (GPa)			
B	189.3	250.0	436.4 (442.0)

direction results in a compression in the transverse direction (to partially conserve volume) giving a positive Poisson ratio. However, for α - C_3N_4 *stretching the crystal in any direction causes it to also expand in the perpendicular directions*. This property results because of the nonplanarity of the nitrogens incorporated as spheroidal cavities into a tetrahedral lattice. No material with a negative Poisson ratio in all directions has previously been reported. α -cristobalite (a form of SiO_2) was reported [25] and confirmed by theoretical calculations [26] to have a negative Poisson ratio for some directions.

5. Summary

Summarizing we predict that

- (i) α - C_3N_4 is more stable than β - C_3N_4 ;
- (ii) both are about half as hard as diamond;
- (iii) α - C_3N_4 has a negative Poisson ratio for all directions; and
- (iv) the observed carbon-nitride films [7] are α - C_3N_4 .

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References

- [1] A.Y. Liu and M.L. Cohen, *Science* 245 (1989) 841.
- [2] A.Y. Liu and M.L. Cohen, *Phys. Rev. B* 41 (1990) 10727.
- [3] C. Niu, Y.Z. Lu and C.M. Lieber, *Science* 261 (1993) 334.
- [4] N. Nakayama, Y. Tsuchiya, S. Tamada, K. Kosuge, S. Nagata, K. Takahiro and S. Yamaguchi, *Japan J. Appl. Phys.* 32 (1993) L1465.
- [5] M.Y. Chen, X. Lin, V.P. Dravid, Y.W. Chung, M.S. Wong and W.D. Sproul, *Tribology Transactions* 36 (1993) 491.
- [6] S. Kumar and T.L. Tansley, *Solid State Commun.* 88 (1993) 803.
- [7] K.M. Yu, M.L. Cohen, E.E. Haller, W.L. Hansen, A.Y. Liu and I.C. Wu, *Phys. Rev. B* 49 (1994) 5034.
- [8] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.W. Wong, J.B. Foresman, M.A. Robb, M. Head-Gordon, E.S. Replogie, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. DeFrees, J. Baker, J.J.P. Stewart and J.A. Pople, *GAUSSIAN 92* (Gaussian, Pittsburgh, 1992).
- [9] M.N. Ringnalda, J.-M. Langlois, B.H. Greeley, T.V. Russo, R.P. Muller, B. Marten, Y. Won, R.E. Donnelly Jr., W.T. Pollard, G.H. Miller, W.A. Goddard and R.A. Friesner, *PS-GVB v1.0*, Schrödinger, Inc., Pasadena, CA 1994.
- [10] W. Nowacki and K. Hedberg, *J. Am. Chem. Soc.* 70 (1948) 1497.
- [11] I. Hargittai and K. Hedberg, *J. Chem. Soc. Chem. Commun.* (1971) 1499.
- [12] R.G. Dickinson and A.L. Raymond, *J. Am. Chem. Soc.* 45 (1923) 22.
- [13] J.A.K. Duckworth, B.T.M. Willis and G.S. Pawley, *Acta Cryst. A* 25 (1969) 482.
- [14] S.L. Mayo, B.D. Olafson and W.A. Goddard III, *J. Phys. Chem.* 94 (1990) 8897.
- [15] W. Meyer and P. Pulay, *Theoret. Chim. Acta* 32 (1974) 253.
- [16] P. Pulay and W. Meyer, *Mol. Phys.* 27 (1974) 473.
- [17] G. Fogarasi and P. Pulay, *Ann. Rev. Phys. Chem.* 35 (1984) 191.
- [18] R.T. Bailey, *Spectrochim. Acta A* 27 (1971) 1447.
- [19] P. Sohar, Z. Zubovics and G.Y. Varsanyi, in: *Molecular structures and vibrations*, ed. S.J. Cyvin (Elsevier, Amsterdam, 1972) p. 359.
- [20] I. Elvebredd and S.J. Cyvin, in: *Molecular structures and vibrations*, ed. S.J. Cyvin (Elsevier, Amsterdam, 1972) p. 283.
- [21] L. Noodleman and N.L. Paddock, *Inorg. Chem.* 18 (1979) 354.
- [22] P. Livant, M.L. McKee and S.D. Worley, *Inorg. Chem.* 22 (1983) 895.
- [23] M.H. Grimsditch and A.K. Ramdas, *Phys. Rev. B* 11 (1975) 3139.
- [24] M. Billy, J.-C. Labbe and A. Selvaraj, *Mat. Res. Bull.* 18 (1983) 921.
- [25] A. Yeganeh-Haei, D.J. Weidner and J. Parise, *Science* 257 (1992) 650.
- [26] N.R. Keskar and J.R. Chelikowsky, *Nature* 358 (1992) 222.