

Carbon(IV) Nitride  $C_3N_4$ —A New Material Harder Than Diamond?

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The prediction of the existence and the structure of previously unknown solid-state compounds seems to be particularly difficult, because numerous complex, interacting factors must be taken into account. A simplification to a certain extent is possible with predominantly covalent polymeric solid-state compounds in which coordination numbers and geometries are unambiguously stipulated for the constituent elements.

Desired properties of new materials are, above all, extreme hardness, good thermal conduction, and high thermal stability. These properties are particularly likely in compounds with highly cross-linked structures with mainly covalent chemical bonds that are very stable. The material property, hardness, can be described by the bulk modulus  $B$ , which, on atomic scale, is influenced fundamentally by the strength and compressibility of the chemical bonds.<sup>[1]</sup> Thus logically, the highest bulk moduli have been found for covalent materials: diamond not only has the highest value (4.43 Mbar), but also is the solid with the greatest hardness.<sup>[1]</sup>

A simple empirical relationship for the estimation of the bulk modulus  $B$  of solids with the zinc blende structure was presented recently by Liu and Cohen [Eq. (a)].<sup>[1]</sup> This pre-

$$B = (19.71 - 2.2 \lambda) / d^{3.5} \quad (a)$$

dicts a dependence of the magnitude of this property on the ionicity  $\lambda$  and the interatomic distance  $d$ . In accord with recent experiments<sup>[2]</sup> this empirical relation yields a bulk modulus for cubic boron nitride that is lower than that of diamond. Furthermore, on the basis of the expression (a), Liu and Cohen predict for a similarly constructed, covalent C–N solid an extremely high mechanical hardness.<sup>[1]</sup>

Of particular significance for the development of novel inorganic materials with interesting properties is the nitride class of substances containing nitrogen as electronegative bonding partner in the oxidation state –III. As a result of its lower electronegativity, nitrogen forms bonds with stronger covalent character as compared to oxygen. Moreover, nitrogen offers more extensive structural possibilities, since it forms not only one or two, but also three or four covalent bonds to neighboring atoms.<sup>[3]</sup> In combination with light main group elements from the p block (e.g., boron, aluminum, silicon, phosphorus), highly cross-linked and predominantly covalent, polymeric solid-state compounds arise.

At present in the group of known binary nitrides of main group elements in which the group number of each corresponds to the maximum oxidation state, a carbon(IV) nitride  $C_3N_4$  is absent. According to the double bond rule, which favors the formation of multiple bonds over the construction of polymeric structures for elements of the second row,  $C_3N_4$  could be assumed to have a molecular structure in the form

of tricyanoazane  $N(CN)_3$ . However, also conceivable in principle and structurally feasible is a polymeric structure analogous to one of the modifications of binary  $Si_3N_4$  with a three-dimensional network structure of  $CN_4$  tetrahedra, sharing corners in all directions. The carbon atoms would be bound covalently to four adjacent carbon atoms like the silicon atoms of  $Si_3N_4$ , while the nitrogen atoms would be coordinated to three tetrahedral centers (C instead of Si) in an almost trigonal-planar arrangement (Fig. 1). Although

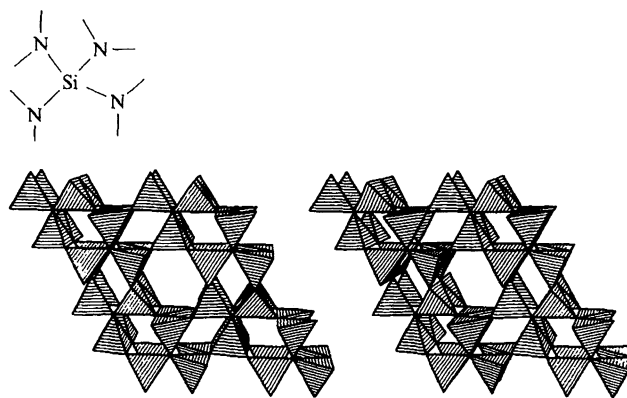


Fig. 1. Bonding and coordination of silicon and nitrogen in  $\beta$ - $Si_3N_4$  (top) and the stereoscopic representation of the crystal structure of  $\beta$ - $Si_3N_4$  viewed along [001] (bottom). The  $SiN_4$  tetrahedra are shown as closed polyhedra. An analogous structure is postulated for  $\beta$ - $C_3N_4$  [4, 8].

no suggestion of the existence of a binary carbon nitride  $C_3N_4$  has yet been found, the cyanamides (e.g.  $Na_2CN_2$ ) are compounds that can be interpreted as ternary carbon(IV) nitrides. In accord with the double bond rule, however, carbon as an element of the second row has been shown to have a lower coordination number ( $CN = 2$ ), so these compounds contain isolated, linear anions  $CN_2^{2-}$ , isosteric with  $CO_2$ .

But is there perhaps also a polymeric  $C_3N_4$  with a structure analogous to  $Si_3N_4$ ? And what material properties might be anticipated for such a compound?

The supposition formulated by Liu and Cohen that solids will have a particularly high bulk modulus when they display short bond lengths and low ionicities, that is, when the compound has a high proportion of covalent bonding, was the starting point for exact theoretical investigations into the potential stability and mechanical properties of binary carbon nitride  $C_3N_4$ . First-principles pseudopotential calculations of the structural and electronic properties (lattice constants, bulk modulus, and electronic band structure) of  $\beta$ - $Si_3N_4$  and its isotype, hypothetical  $\beta$ - $C_3N_4$ , were in good agreement with experimental data obtained from silicon nitride. Two significant statements about  $C_3N_4$  can be made: The bulk modulus of this compound should be comparable with that of diamond. Moreover,  $\beta$ - $C_3N_4$  should be able to be synthesized, at least as a metastable form under normal conditions, because of its moderately large cohesive energy.

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As regards thermodynamic stability,  $\beta$ - $C_3N_4$  therefore fits into the series of other superhard materials, that, like diamond or cubic boron nitride, are also only metastable under normal conditions.

Efforts of various groups to synthesize a binary carbon nitride with a  $\beta$ - $C_3N_4$  structure initially yielded no indication that a polymeric solid containing carbon atoms tetrahedrally surrounded by nitrogen atoms exists.<sup>15-71</sup> These experiments employed, in particular, plasma deposition from  $CH_4/N_2$  mixtures and pyrolytic decomposition of organic C-N-H compounds. Also shock wave compression in pyrolysis products of melamine-formaldehyde resins did not bring the desired success. Considerably more promising were the recently published studies of Niu, Lu, and Lieber,<sup>18</sup> in which synthetic methods are presented that generate both highly energetic carbon species as well as atomic and reactive nitrogen. The product was obtained by trapping of the resultant C-N products by low-temperature thin-film growth. The generation of the highly energetic carbon species takes place through the ablation of a very pure graphite target with a Nd:YAG laser. Atomic nitrogen with high kinetic energy ( $>1$  eV) was generated by radio frequency discharge in a high-flow stream of He- $N_2$ .

C-N films containing different nitrogen content were obtained with this process. Quantitative analysis of the reaction products with Rutherford back-scattering spectroscopy (RBS) revealed nitrogen contents in the studied samples of maximally 45%. This value lies distinctly below the theoretical value of 57% for  $\beta$ - $C_3N_4$ . Moreover, it has been shown that a C-N solid with a nitrogen content worth mentioning can be constructed only when atomic nitrogen is introduced during the sputtering process. X-ray photoelectron spectroscopy (XPS) of the samples gave clear evidence for non-polarized, covalent bonds between carbon and nitrogen. Transmission electron microscopic investigations (TEM) showed at first a pure crystallinity in the sputtered C-N films; however, small crystallites with grain sizes of less than 10 nm were detected. The diffraction pattern obtained under the electron microscope was readily observed to be consistent with the assumption of a structure analogous to  $\beta$ - $Si_3N_4$  having the lattice constants determined theoretically for  $\beta$ - $C_3N_4$ . The remarkable material properties of  $\beta$ - $C_3N_4$  predicted by theoretical studies were able to be confirmed, at

least qualitatively: the material showed a high thermal and mechanical stability.

Certainly one cannot yet speak of the synthesis of a defined, crystalline carbon nitride of composition  $C_3N_4$  amongst the C-N layers of Niu, Lu, and Lieber. Nevertheless, the but short history of these compounds is remarkable: Whereas, for instance, in Gmelin's Handbook of Inorganic Chemistry a compound of the composition  $C_3N_4$  is not even mentioned, simple empirical studies lead to the assumption that such a C-N solid should have particularly attractive material properties (exceptional hardness). This qualitative statement is confirmed by ab initio calculations. Simultaneously, an adequate stability is claimed that makes synthesis of  $C_3N_4$  feasible, at least in metastable state. After some unsuccessful preparative attempts a process was finally developed to circumvent the former thermodynamic problems in the formation of  $C_3N_4$  through the generation of highly reactive carbon species and atomic nitrogen. The solid, which is formed in a potentially metastable state is stabilized kinetically by growth at low temperatures.

Apparently the difficult prediction of the existence and structure of a previously unknown solid-state compound and its experimental verification has indeed been achieved. The results are certainly stimulating both for materials research and for solid-state chemistry. It will inspire a whole series of further preparative efforts and investigations. After all, not only is the preparative route to a new binary nitride of one of the most important main group elements attractive, but also the synthesis and applications of a new material with potentially particularly desirable properties. As with other binary nonmetal nitrides, the question of an extensive chemistry in the form of ternary and higher compounds also arises (cf. [9]).

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