Silicon Boron Nitrides: Hypothetical Polymorphs of $Si_3B_3N_7$**

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Materials based on silicon boron carbon nitrides (Si-B-(C)-N) are intriguing potential "ultra high temperature materials", combining thermal stability at temperatures of 1700 °C and above[1, 2] with remarkable resistance to oxidation.[3, 4] Recent reviews on their synthesis by polymer-to-ceramic transformations are given by Riedel et al. and by Baldus and Jansen.[5, 6] In particular, Baldus and Jansen concentrated on the synthesis of two stoichiometric compounds, $Si_3B_3N_7$ and $SiBCN_3$. As a consequence of the synthesis from single source precursors, these ternary and quarternary Si-B-(C)-N compounds are homogeneous down to the length scale of current high-resolution transmission electron microscopy (ca. 10 Å). What impedes structural investigations is the fact that these compounds are amorphous.

We do know something of the local enviroment of the atoms. In $Si_3B_3N_7$ the boron atoms are locally coordinated as in hexagonal BN, that is, approximately threefold planar coordinated by nitrogen atoms.[6] The local enviroment of silicon is similar to that in Si_3N_4 (α or β phase), approximately tetrahedrally coordinated by four nitrogen atoms. The local enviroment of nitrogen is threefold (planar), and appears to consist of a mixture of N–B and N–Si bonds. Given the structure of the molecular precursor[7] and the synthetic method, Si–Si, B–B, N–N as well as Si–B bonds appear unlikely.

Since the properties of compounds depend ultimately on their geometrical and electronic structure, we set out in search of translationally periodic three-dimensional covalent inorganic networks which would satisfy the experimentally found bonding topology and thus serve as models for amorphous $Si_3B_3N_7$ and $SiBCN_3$. Here, we restrict ourselves to $Si_3B_3N_7$ models. One such structure has been suggested by Schön and Jansen.[8] We show that hypothetical structures for $Si_3B_3N_7$ can be derived in principle from any alternating 3/4-connected net of stoichiometry A_3B_4.[9]

To illustrate our approach, consider the structure of α-Si_3N_4 (**1**, Figure 1), which is composed of tetrahedral silicon atoms and almost trigonal-planar nitrogen atoms. Imagine removing one nitrogen atom. This will leave three silicon atoms, each with one "dangling bond" (**2**). If we replace these silicon atoms with boron, each boron atom will be bonded to three nitrogen atoms (**3**). Of course, the boron atom is initially pyramidal, but this will change during a subsequent relaxation of the structural parameters (**4**).

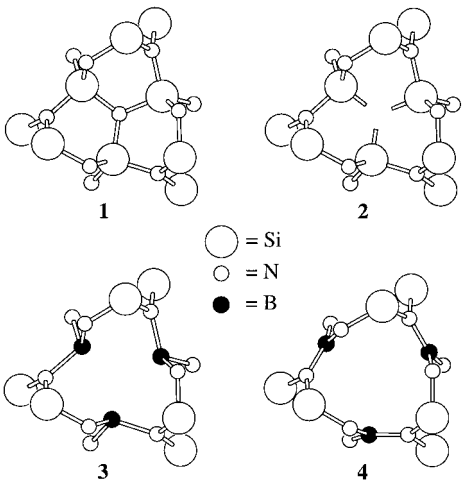

Figure 1. Illustration of the discarding/replacing procedure; the cluster model shown is an example taken from α-Si_3N_4 (**1**) in which a nitrogen atom is removed (**2**), and three silicon atoms are replaced by boron (**3**). Relaxation of **3** leads to **4**.

Let us see how the stoichiometry is affected by this construction. Every time we discard one nitrogen atom, we replace three silicon atoms with boron.[10] If we start with a composition $Si_{3Z}N_{4Z}$, where Z is the number of formula units in the repeated cell, after the nth repetition of the protocol described we reach a stoichiometry $Si_{3Z-3n}B_{3n}N_{4Z-n}$. Therefore, if we want to create a Si-B-N network with a ratio of silicon to boron atoms of k_{Si}/k_B, the parent 3/4-connected network should have $Z = n((k_{Si}/k_B) + 1)$ units of Si_3N_4. The value of n has to be chosen to make Z an integer. Clearly a complete range of Si/B ratios is accessible with this procedure, and the amount of nitrogen in an Si-B-N phase depends explicitly on this ratio.

Our search for possible parent networks for the generation of $Si_3B_3N_7$ structures began with both silicon nitride structures. Since we limited ourselves to structures with 13 or 26 atoms in the unit cell ($Z \leq 2$), we could derive 3 candidates from β-Si_3N_4 (one with $Z = 1$) and 14 candidates from α-Si_3N_4 (all with $Z = 2$). Enlarging the basis of parent networks to further alternating 3/4-connected nets increases the number of distinct $Si_3B_3N_7$ structures with $Z \leq 2$ to more than 100.[11, 12] We analyzed all nets through their coordination sequences and extended Schläfli symbol[13] and found that each parent network generates $Si_3B_3N_7$ networks distinct from those derived from other parent structures. In our calculations we also included the one structure suggested for $Si_3B_3N_7$ that has been published previously.[8]

A detailed description of all the nets is not possible here, but we mention the extensive variety of boron–nitrogen substructures observed. Common zero-dimensional motifs are the BN_3 or $N(BN_2)_3$ molecular units as well as 6- and 12-membered BN rings. A prevalent one-dimensional motif is a BN chain, which is more or less distorted from an ideal, polyacetylene-like configuration. Structures with two-dimensional BN subnets are also found. Moreover, the reduced mean connectivity (42/13 = 3.23) in comparison to a four-

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connected net even allows the construction of two-dimensional $Si_3B_3N_7$ structures.

With over 100 structures for $Si_3B_3N_7$ derived by our construction principle, we faced the problem of identifying those with lowest energy. First we concentrated on the structures derived from α- and β-Si_3N_4. To broaden our investigation we also viewed structures derived from willemite-II,[14] sphalerite, γ-Si, the boron subnet in CrB_4, and MAPO-39 structures.[15] The ground-state properties of the structures were calculated with use of standard density functional theory methods with full geometry optimization.[16] Table 1 gives a summary of the results for selected $Si_3B_3N_7$ structures. Many other structures are more than 1.9 eV per formula unit less stable than the lowest energy structure. The two $Si_3B_3N_7$ structures lowest in total energy, α-1-$Si_3B_3N_7$ and β-2-$Si_3B_3N_7$, are derived from α-Si_3N_4 and β-Si_3N_4.

Note that all computed $Si_3B_3N_7$ structures (except a high-pressure phase γ-hp) are less dense than Si_3N_4, having only 85–90% of the density of the parent structure. For example, the density of α- and β-Si_3N_4 is about 3.3 g cm^{-3}, whereas $Si_3B_3N_7$ structures derived from these structures have a density between 2.8 and 2.9 g cm^{-3} (Table 1). The reason for this is the protocol in which nitrogen is removed and silicon is substituted by boron, which is only partially compensated by a decrease in the volume of the unit cell. The $Si_3B_3N_7$ phase with lowest density (ca. 2.5 g cm^{-3}), but high energy, was derived from the zeolite net MAPO-39.[17]

Looking at the structural details (not reported here) we find the following: 1) Boron always relaxes to be approximately planar. The sum of angles at boron deviates less than 3.5° from 360° (the ideal planar configuration). The bond angles at boron are close to 120° with a maximum deviation of 6°. 2) Nitrogen also tends to be planar, although the preference is less expressed than for boron. For structures derived from α- or β-Si_3N_4 the minimum sum of angles at the nitrogen site is 340° (in α-3), which indicates somewhat pyramidal coordination. For structures derived from other parent 3/4-connected nets the deviation from planarity is even higher. Bond angles at nitrogen scatter in the range between 100 and 140°.

The structure of β-2-$Si_3B_3N_7$, which has a clear resemblance to that of β-Si_3N_4, is shown in a ball-and-stick model in Figure 2. The boron atoms relax towards the center of the big channels as they become planar; the channels are built from stacked $[(Si_6N_6)(B_6N_6)]$ sequences and are connected through the silicon atoms by additional nitrogen atoms. In molecular

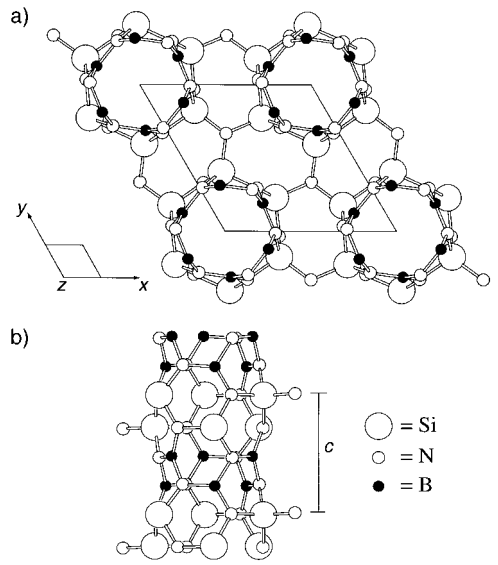

Figure 2. Ball-and-stick model of the structure of β-2-$Si_3B_3N_7$. a) Projection on to the xy plane, which makes the resemblance to β-Si_3N_4 clear. b) View perpendicular to the z axis. Columnar $Si_3B_3N_6$ tubes are linked by additional nitrogen atoms.

chemistry the large 12-membered B_6N_6 ring is known only as part of a macrocycle.[18] In the 12-membered B_6N_6 ring of β-2-$Si_3B_3N_7$ the calculated B–N distances are 1.43 and 1.47 Å.[19] The computed bond angles N-B-N and B-N-B are 117.1 and 114.6°, respectively; the dihedral angles N-B-N-B and B-N-B-N are 14.5 and 112.2°, respectively.

In Figure 3 we show the structure of α-1-$Si_3B_3N_7$. Intriguing here is the motif of one-dimensional chains of B and N atoms, an inorganic analogue of polyacetylene. The B–N distances inside the chains are 1.486 and 1.492 Å. The chains are slightly deformed and twisted relative to an idealized geometry; the N-B-N and B-N-B angles are 126.1 and 123.2°, respectively; and the dihedral angles N-B-N-B and B-N-B-N are 160.7 and 159.5°, respectively.[20]

How hard might these materials be? We calculated the bulk modulus for various structures.[21] It turned out that α-1-$Si_3B_3N_7$ is the phase with the highest bulk modulus (Table 1). It is also the only phase where the bulk modulus (2.4 Mbar) is comparable to that of silicon nitride (α-Si_3N_4: 2.4, β-Si_3N_4: 2.55 Mbar). Our calculations furthermore revealed a high-pressure phase γ-hp, which should be energetically more favorable at pressures of about 20 GPa. This γ-hp phase is about 20% more dense than β-2-$Si_3B_3N_7$. As in the cubic

Table 1. Space group, number of formula units in the unit cell (Z), volume (per formula unit $Si_3B_3N_7$; V_0), density (ρ), relative energy (ΔE_0), and bulk modulus (B_0) for selected hypothetical phases of $Si_3B_3N_7$. The α and β structures are derived from α-Si_3N_4 and β-Si_3N_4, respectively. The numerals after the structure abbreviation are from an arbitrary numbering of structures in the class; sj is the $Si_3B_3N_7$ structure given in reference [8]. γ-hp is a high-pressure phase of $Si_3B_3N_7$ with a different bonding topology (see text). The total energy is given per $Si_3B_3N_7$ formula unit and relative to that of β-2-$Si_3B_3N_7$ (−2468.0 eV).

Phase	β-1	β-2	α-1	α-3	α-4	sj	γ-hp
space group	$P\bar{6}$ (176)	$P\bar{3}$ (147)	$P31c$ (159)	$P3$ (143)	$P3$ (143)	$P1$ (1)	$R3$ (146)
Z	1	2	2	2	2	1	1
V_0 [Å^3]	126.5	127.8	123.9	126.5	124.4	128.7	101.3
ρ [g cm^{-3}]	2.82	2.79	2.88	2.82	2.87	2.77	3.52
ΔE_0 [eV]	1.0	[0]	0.2	1.1	0.4	1.2	2.3
B_0 [MBar]	1.9	2.0	2.4	2.1	2.3		2.7

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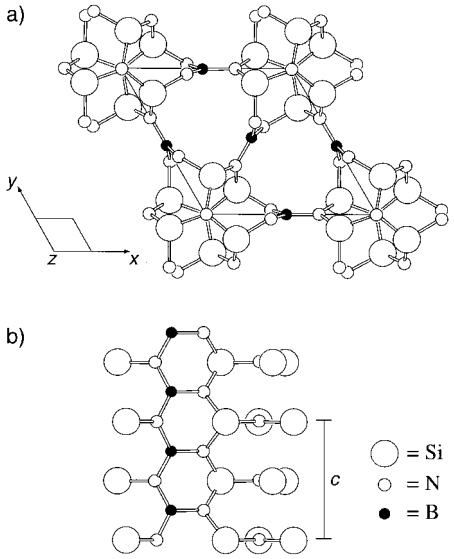

Figure 3. Ball-and-stick model of the structure of α-1-$Si_3B_3N_7$. a) Projection on to the *xy* plane. b) View perpendicular to the *z* axis showing one-dimensional chains formed by B and N atoms.

phase of boron nitride, we can find four-connected boron and nitrogen atoms in γ-hp. Since the number of tetrahedral sites in this structure is higher than in the others we considered for $Si_3B_3N_7$, we expect this structure to be more rigid. And indeed we found the bulk modulus to be 2.7 MBar, which is 10% higher than that computed for α-1-$Si_3B_3N_7$.

All structures we calculated are semiconductors with wide band gaps (typical band gap: 4–6 eV (local density approximation, LDA)), as expected from the network topology and the difference in electronegativity of the elements. A crystal orbital overlap population[22] analysis of Si–N and B–N bonds in α-1- and β-2-$Si_3B_3N_7$ revealed that these bonds are quite similar, as expected, to those in the corresponding binary compounds Si_3N_4 and h-BN.

Our final result concerns the energetics of decomposition of $Si_3B_3N_7$. We calculated the total energies for β-Si_3N_4 and h-BN to obtain the energy for the reaction $Si_3B_3N_7 \rightarrow \beta$-$Si_3N_4 + 3\,BN$. The resulting $\Delta E \approx -1.7$ eV (approximately 0.1 eV per atom) suggests that $Si_3N_3N_7$ is not thermodynamically stable at low temperatures. At elevated temperatures the entropy contribution to the free energy might lower this difference or even change the sign of ΔE. The energetically most favorable structures, β-2-$Si_3B_3N_7$ and α-1-$Si_3B_3N_7$, are at least mechanically stable.[23] If they are synthesized, they will encounter a substantial kinetic barrier to their decomposition.

In summary, we have illustrated a construction principle for structures of the formula $Si_{3Z-3n}B_{3n}N_{4Z-n}$ and examined the structure and energetics of many candidate structures for ordered $Si_3B_3N_7$. Full geometrical optimization of the structures reveals that boron atoms with planar coordination and nitrogen atoms with nearly planar coordination are characteristic of the low-energy structures. The two lowest energy structures are about 15% less dense than Si_3N_4, but exhibit comparable mechanical properties. Although none of the hypothetical ordered phases we showed has been synthesized so far, we are convinced that the covalent network of amorphous $Si_3B_3N_7$ and one or more of the more stable hypothetical phases described here will resemble one another.

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[9] In an alternating 3/4-connected net every four-connected vertex is linked to four three-connected vertices and every three-connected vertex is linked to three four-connected vertices. Rings with an odd number of atoms are thus excluded. Since silicon will be tetrahedrally coordinated, we rule out parent nets with a square-planar four-connected vertex, such as that proposed for Pt_3O_4.
[10] The nitrogen atom which is to be discarded must not be already bonded to a boron atom.
[11] A more rigorous approach to the search for $Si_3B_3N_7$ polymorphs is provided by a graph theoretical approach (see e.g.: M. Bader, W. E. Klee, G. Thimm, *Z. Kristallogr.* **1997**, *212*, 553–558). This procedure may be rather cumbersome to apply here, since the stoichiometry $Si_3B_3N_7$ requires at least 13 vertices in the unit cell, and a huge number of labeled graphs would result (a combinatorial explosion: M. M. Treacy, K. H. Randall, S. Rao, J. A. Perry, D. J. Chadi, *Z. Kristall.* **1997**, *212*, 768–791).
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[17] To our knowledge the density of amorphous $Si_3B_3N_7$ has not been reported so far. The density of $SiBCN_3$ is about 1.8–2 g cm^{-3}.[6]
[18] a) I. Haiduc, R. B. King in *Large Ring Molecules*, (Ed.: J. A. Semlyen), Wiley, **1996**, pp. 525–597; b) A. Meller, H.-J. Füllgrabe, *Angew. Chem.* **1975**, *87*, 382–383; *Angew. Chem. Int. Ed. Engl.* **1975**, *14*, 359–360.

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[19] For comparison: We computed the B–N bond length in hexagonal boron nitride as 1.436 Å, in cubic boron nitride as 1.547 Å. The experimental values are 1.446 and 1.565 Å, respectively (K.-H. Hellwege, A. M. Hellwege in *Landolt-Börnstein, New Series, Group III, Vol.* 7, *Crystal Structure Data of Inorganic Compounds, Part C*, Springer, Berlin, **1978**).

[20] For both structures, β-2-$Si_3B_3N_7$ and α-1-$Si_3B_3N_7$, the mean Si–N bond distance is 1.715 Å, with very small deviations. This is nearly exactly the same as computed for α-Si_3N_4 and β-Si_3N_4, 1.713 and 1.716 Å, respectively (experimental values: 1.738 Å (I. Kohatsu, J. W. McCauley, *Mat. Res. Bull.* **1974**, *9*, 917–920) and 1.732 Å (R. Grün, *Acta Crystallogr. Sect. B* **1979**, *35*, 800–804), respectively).

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[23] The calculation of the elastic constants for both structures revealed that they meet the Born criteria for mechanical stability (positive definite stiffness matrix). Thus, the structures are stable against strain. The actual values will be given in a full paper; they are comparable to those of β-Si_3N_4.

Modeling of Benzene Adsorption in Metal-Exchanged Zeolites by Calculation of ^{7}Li Chemical Shifts**

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Metal-exchanged zeolites are important adsorbents and catalysts, and NMR spectroscopy is commonly used to determine the structure and dynamics of complexes formed between adsorbates and metal cations in zeolites, but such studies usually focus on ^{2}H or ^{13}C nuclei in the organic species. Adsorbate-induced changes in the chemical shifts have been observed for ^{133}Cs nuclei in zeolites,[1] but ^{133}Cs has an exceptionally large chemical-shift range and may not be representative. At the other extreme is lithium, which has a very modest chemical-shift range. If the ^{7}Li or ^{6}Li chemical shift were sensitive to adsorbate complexation, the effect might be generally useful, especially when quadrupolar effects can either be ignored (as for the central transition of ^{7}Li at moderate fields) or separated from the chemical shift.[2]

Magic angle spinning (MAS) ^{7}Li NMR spectra of zeolite LiZSM-5 suggest almost quantitative titration of the ^{7}Li resonance with 0.9 equivalents of benzene (Figure 1). The ^{7}Li isotropic chemical shift of the evacuated zeolite is $\delta = -0.2$ at 298 K, and adsorption of benzene results in discontinuous movement of the ^{7}Li signal to $\delta = -3.5$ ($\Delta\delta = -3.3$). The spectra appear to be in the slow-exchange regime of benzene hopping between cation sites. The ^{7}Li MAS NMR spectrum of the sample with 0.6 equivalents of benzene was recorded as a function of temperature. Coalescence of the two isotropic signals was observed in the vicinity of 493 K (not shown).

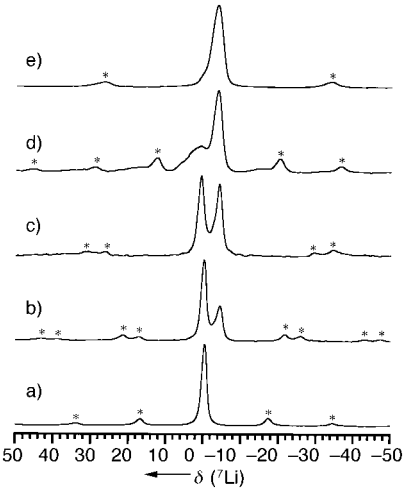

Figure 1. ^{7}Li MAS NMR spectra (116.5 MHz) of LiZSM-5 with the following benzene loadings: a) 0.0, b) 0.4, c) 0.6, d) 0.9, e) 2.0 equiv. Spinning sidebands are indicated by an asterisk.

Aromatic adsorbates such as *p*-xylene produce changes in the ^{29}Si chemical shifts of ZSM-5 zeolites by inducing a phase transition between polymorphs.[3] Here we present theoretical calculations which confirm that the changes in the ^{7}Li chemical shift above are indeed the result of 1:1 complexation between Li^+ and benzene, and not other effects.

Cation–π interactions have been studied both experimentally and theoretically, and have been recently reviewed.[4] In gas-phase calculations, Li^+ forms both 1:1 and 1:2 complexes with benzene. These are more strongly bound than analogous complexes of the other alkali metal cations. Cation–π interactions in aqueous solution have also been studied theoretically to model their roles in biochemical processes (e.g., ion-channel selectivity).[5]

We used ab initio methods to quantitatively model the experimental observations of Figure 1. We used the GIAO-MP2 method[6–8] to explore how the ^{7}Li chemical shift changes when Li^+ ions are π-complexed by benzene or when they are coordinated to various other ligands. Full geometry optimizations were performed at the MP2/6-311+G* level (Figure 2). We used Li^+, LiH, $Li^+ \cdot H_2O$, and $Li^+ \cdot 2H_2O$ as simplified models of the uncomplexed site. Additionally, we optimized a complex of Li^+ with two benzene molecules. Because of computational costs, we did not include larger, more realistic models of Li sites, such as $Li^+ \cdot 3H_2O$.

The chemical shifts of the structures in Figure 2 were calculated at the GIAO-MP2 level (Table 1). The ^{7}Li chemical shift is relatively insensitive to the basis set on C; in each case the ^{7}Li shift moved downfield (more positive) by 0.2 ppm when the basis on C was reduced from tzp to dzp (see Experimental Section). The isotropic ^{13}C shift moved downfield by only $\Delta\delta = 3.7$ when benzene was complexed with Li^+, which is in agreement with experiment. Smaller effects were

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