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Borazine based molecular single source precursors for Si/B/N/C ceramics

Fanny Schurz^[a] and Martin Jansen^{*[a]}*Dedicated to Professor Gerd Becker on the Occasion of his 70th Birthday***Keywords:** Borazine; Si/B/N/C Ceramic; Crystal Structure; Polymerization

Abstract. The family of borazines [(SiCl₃)NB(Cl_n(CH₃)_{1-n})₃] has been synthesized and characterized by NMR and IR spectroscopy, as well as by single crystal structure analysis. After crosslinking with methylamine, a soluble polymer was obtained, which was transformed to an all-inorganic random network of nominal compo-

sition Si_{1.0}B_{1.0}N_{3.0}C_{0.9}O_{0.1} (idealized SiBN₃C) at 1400 °C. With an on-set of weight loss at 1840 °C and a resistance against rapid oxidation in pure oxygen of up to 1300 °C, the new Si/B/N/C ceramic shows a high temperature performance similar to those of previously reported Si/B/N/C materials.

Introduction

Random networks consisting of Si, B, N, and C represent a new class of ceramics that are exclusively accessible along a molecular – polymer precursor route [1–7]. Single source molecular precursors of the general type R₁R₂R₃Si-X-BR₄R₅ with X = NH [1, 8–10], N(CH₃) [11–13], CH₂ [14, 15], C₂H₄ [16] and R₁-R₅ = CH₃ or Cl have proven to perform particularly well with respect to versatility and quality of the final ceramic. As measured by the combination of properties relevant for an application as structural ceramics at high temperature, the Si/B/N/C ceramics show superior performance [6]. In particular its creep resistance and stability in oxygen (compared to the other non – oxide ceramics) is without precedent [6]. By applying various analytical probes, the basic structural features have been revealed. Silicon is in a tetrahedral coordination by nitrogen, while boron is in a trigonal planar surrounding of nitrogen. Carbon is not bonded to either of the cations, but forms sub-nanometer aromatic carbonaceous regions that are exclusively linked to nitrogen [17]. Furthermore, there are small segregations of Si/N and B/N, again of sub-nanometer size [18]. This is implying that planar, borazine type structural elements should be present. We regard this sub-nanometer microstructure in combination with the underlying network of strong, highly cross-linked bonds the reason for the pronounced stability of the Si/B/N/C ceramics [18].

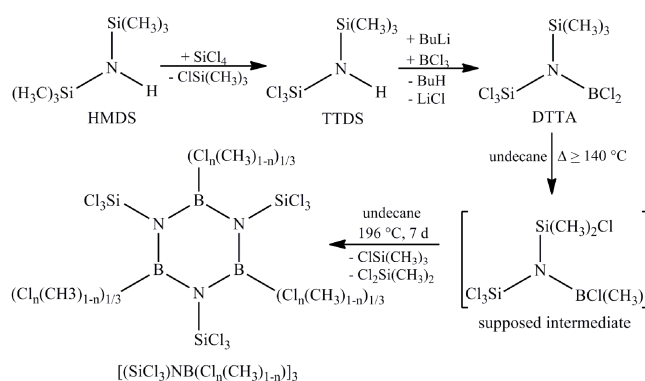
Against the background of the structural features mentioned, it has appeared reasonable to generate such random networks starting from molecular precursors that contain borazine units right from the beginning. In the borazine based precursors studied so far, boron and silicon are linked by carbon atoms or chains [19–21], which is a

linkage that is not constitutive of the first generation of Si/B/N/C ceramics. Thus, during the process of condensing a respective polymer by pyrolysis manifold rearrangements of B-C and Si-C bonds would be required, most probably resulting in a higher concentration of dangling bonds. Therefore we have regarded it worthwhile to use molecular precursors, in which silicon is attached to a borazine core by nitrogen bridges. Here we report on the borazine derivatives [(SiCl₃)NB(Cl_n(CH₃)_{1-n})₃], their characterization and transformation to an amorphous inorganic Si/B/N/C ceramic.

Results and Discussion

Synthesis and characterization of monomer [(SiCl₃)NB(Cl_n(CH₃)_{1-n})₃]

The synthesis of the borazine derivative [(SiCl₃)NB(Cl_n(CH₃)_{1-n})₃] (Scheme 1) consists of three steps starting with the transilylation on hexamethyldisilazane (HMDS) to obtain 1,1,1-trichloro-3,3,3-trimethyldisilazane (TTDS). In the following step the proton in TTDS is replaced by a dichloroboryl group using butyl lithium (BuLi) and BCl₃ resulting in dichloroboryl-(trichlorosilyl)-(trimethylsilyl)-amine (DTTA). DTTA is converted by a

Scheme 1 Synthesis route of [(SiCl₃)NB(Cl_n(CH₃)_{1-n})₃].

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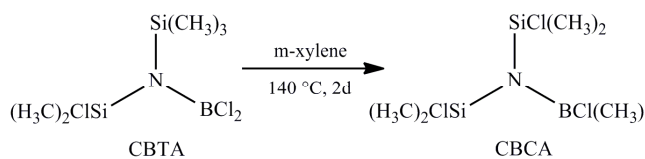
thermally induced silazane cleavage in boiling undecane at 196 °C into the borazine derivatives $[(\text{SiCl}_3)\text{NB}(\text{Cl}_n(\text{CH}_3)_{1-n})]_3$ which are obtained as colorless, prismatic, layered pads.

At preparation conditions, which had proven suitable for the synthesis of $[(\text{Si}(\text{CH}_3)\text{NBCl}_2)_3]$ [22], using *m*-xylene as solvent and reaction temperatures of 140 °C, our target molecule could not be obtained. Only at temperatures above 170 °C the latter borazine derivatives formed while the yield is dependent on the reaction temperature and time. Unexpectedly, to the boron atoms of the resulting borazine derivatives chlorine atoms as well as by methyl groups are bonded in a random fashion, and that in a ratio of close to 1 : 2. This is the result of a thermally induced substituents exchange among the BCl_2 and $\text{Si}(\text{CH}_3)_3$ groups of DTTA during the last synthesis step, leading to the formation of $\text{BCl}(\text{CH}_3)$ and $\text{SiCl}(\text{CH}_3)_2$ functionalities, next to SiCl_3 groups. In the following silazane cleavage of the N – $\text{SiCl}(\text{CH}_3)_2$ bond, both, a chlorine as well as a methyl group can be cleaved from the boron atom to form dichlorodimethylsilane or chlorotrimethylsilane as side-products. The exchange of the substituents is observed to occur at temperatures above 140 °C. In order to corroborate the mechanism suggested we have studied dichloroboryl-(chlorodimethylsilyl)-(trimethylsilyl)amine (CBTA) as a model system: CBTA converts in boiling *m*-xylene (140 °C, 2d) into chloromethylboryl-bis(chlorodimethylsilyl)-amine (CBCA) as the only product (Scheme 2). Further, the role of the $\text{Si}(\text{CH}_3)_3$ group acting as a methylation agent is supported by the fact that alkylated silanes [23] as well as tris(trimethylsilyl)-amine [24, 25] react in an analogous way with halogenated boranes.

It was not possible to separate the obtained borazine derivatives $[(\text{SiCl}_3)\text{NB}(\text{Cl}_n(\text{CH}_3)_{1-n})]$ by sublimation, although they are bearing different numbers of methyl groups. Such a separation problem has been encountered in similar cases, e. g. for the mixtures of $\text{SiCl}_4 / (\text{CH}_3)_3\text{SiCl}$ in which boiling points are 57.6 °C / 57 °C, as well as for $(\text{SiCl}_3)\text{-N}(\text{CH}_3)\text{-BCl}_2 / (\text{SiCH}_3)_3\text{-N}(\text{CH}_3)\text{-BCl}_2$ [26].

The mass spectrum of the product mixture (Figure 1) does not show the molecular ion peaks of the expected borazine derivatives, m/z $[(\text{SiCl}_3)_3\text{N}_3\text{B}_3\text{Cl}_3]^+ = 584$, m/z $[(\text{SiCl}_3)_3\text{N}_3\text{B}_3\text{Cl}_2(\text{CH}_3)]^+ = 564$, m/z $[(\text{SiCl}_3)_3\text{N}_3\text{B}_3\text{Cl}(\text{CH}_3)_2]^+ = 543$, m/z $[(\text{SiCl}_3)_3\text{N}_3\text{B}_3(\text{CH}_3)_3]^+ = 523$. They fragment by the loss of chlorine atoms and methyl groups (Scheme 3).

By ^{11}B NMR spectroscopy two different chemical environments of boron atoms are proven. In the ^1H NMR spectrum two signals, both in the range of the chemical shift of B- CH_3 groups, with an intensity ratio of nearly 1 : 1, confirm the formation of different borazine derivatives in the sample. Due to the quadrupol moment of boron the signals in the ^{13}C NMR are very broad (between 10 and 12 ppm) and do not allow for clear conclusions. The chemical



Scheme 2 Conversion of CBTA into CBCA by intramolecular substituent exchange.

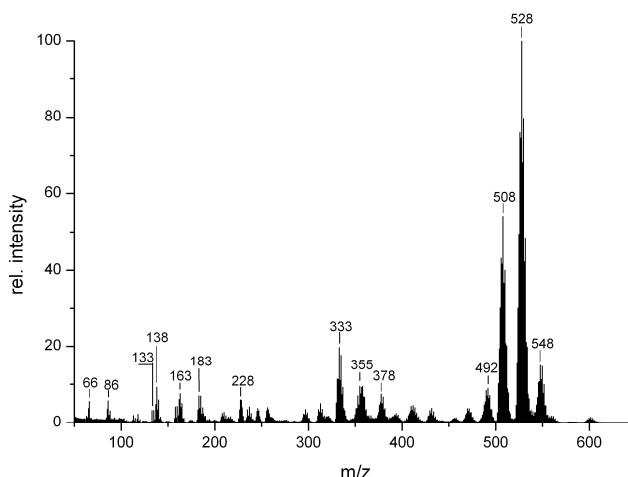
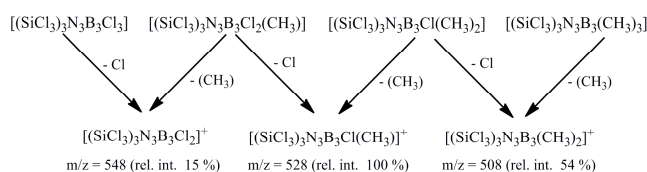


Figure 1 Mass spectrum of $[(\text{SiCl}_3)\text{NB}(\text{Cl}_n(\text{CH}_3)_{1-n})]_3$ (60 eV).



Scheme 3 Fragmentation of the borazine derivatives (60 eV).

shift of the SiCl_3 groups in the ^{29}Si NMR spectrum is in the expected range and a distinctive coupling between ^{29}Si and ^{14}N is detectable.

The FT-IR spectrum of the borazine derivatives (Figure 2) shows very intense absorptions at 1279 and 1336 cm^{-1} , which we assign to the antisymmetric stretching vibration of the BN and BN_2 units of the borazine ring. The bands at 588 and 610 cm^{-1} are generated by the SiCl_3 groups whereas the stretching mode of the Si-N bond is detectable at 910 cm^{-1} . A weak absorption at 2962 cm^{-1} assigned to the stretching vibration of CH_3 groups evidences the presence of $\text{B}(\text{CH}_3)$ bonds.

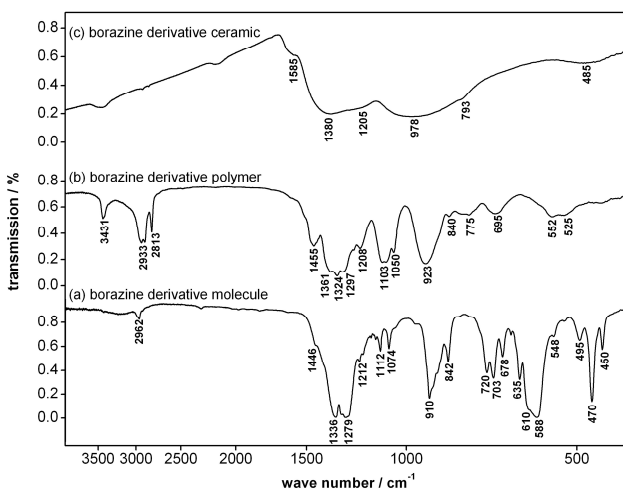


Figure 2 FT-IR spectra of (a) the borazine derivatives $[(\text{SiCl}_3)\text{NB}(\text{Cl}_n(\text{CH}_3)_{1-n})]_3$, (b) the derived polymer and (c) the derived ceramic.

The constitution of the obtained borazines as determined spectroscopically has been confirmed by single crystal structure analysis (Table 1, Figure 3). As a striking feature, though not unique, the B_3N_3 – core of the molecule is not planar but in a chair conformation (Figure 3). The site symmetry m of $[(SiCl_3)NB(Cl_n(CH_3)_{1-n})]_3$ allows for two independent dihedral angles $N1B1N1' - N1N1'B2B2'$ and $B2N2B2' - N1N1'B2B2'$, amounting to 20.6° and 21.4° , respectively. Other examples of borazine derivatives with a non-planar hetero-cycle are known including such with a chair $[(SiMe_3)NCl]_3$ [22], a boat $[(Ph_3Ge)Me_2B_3N_3]Pr_3$ [27] or a twist $[PhF_2B_3N_3]Bu_3$ [28], $\{[EtBNCl]_3Cr(CO)_3\}$ [29], $[Me_3B_3N_3H_2Ti(OtBu)_3]$ [30] conformation. The non-planarity can be caused by the presence of voluminous substituents attached to the borazine ring as well as by the electronegativity of the nitrogen bonded groups. In contrast, all borazine based Si/B/N/C precursors reported, thus far, ($\{[(SiCl_3)CH_2]BNH\}_3$ [31], $\{[(SiCl_2Me)CH_2]BNH\}_3$ [31] and $\{(SiCl_3)C_2H_3\}BNH\}_3$ [32]) are planar.

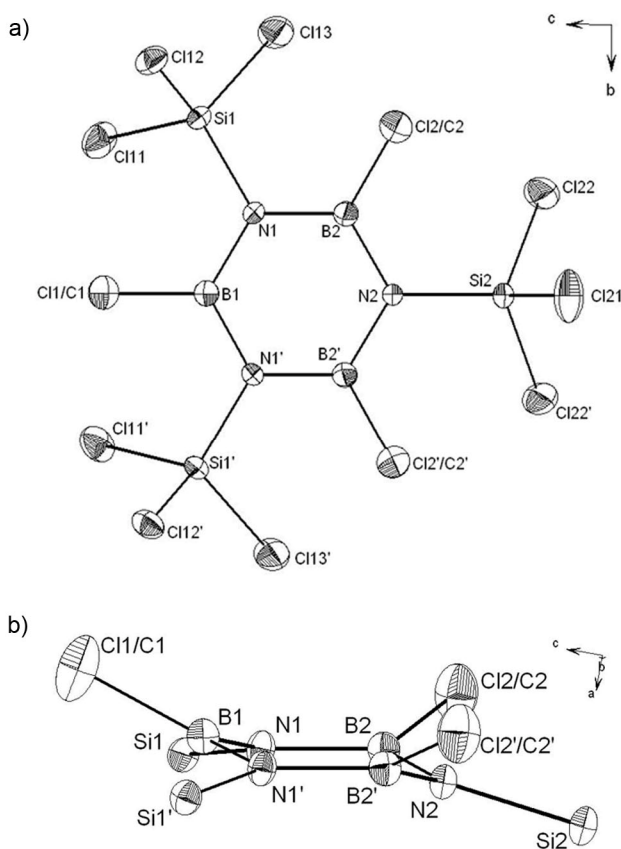


Figure 3 Structure of $[(SiCl_3)NB(Cl_n(CH_3)_{1-n})]_3$, a) top view; b) side view (only the atoms directly bonded to the ring atoms are shown) of the borazine heterocycle.

All B-N bonds of the borazine ring have nearly the same length of 1.45 \AA (Table 2) that indicates a partial double bonding character like in 2,4,6-trimethylborazine (1.38 \AA [33]), in 2,4,6-trichloroborazine $[HNCl]_3$ (1.41 \AA [34]) and in borazine $[HNBH]_3$ (1.43 \AA [35]) as well as in $[(Si(CH_3)_3)NCl]_3$ (1.43 \AA [22]). While the positions of the nitrogen bonded $SiCl_3$ substituents were fully resolved, showing all pertinent distances and angles in the expected ranges (Table 2), the coincidences of the B-Cl and B- CH_3

groups of the individual molecules necessitate the splitting of the 4c site for Cl1/C1 and of the 8d site for Cl2/C2 leading to site occupation factors 0.180(3) for Cl1, 0.319(3) for C1, 0.370(4) for Cl2 and 0.629(4) for C2. So, it was only possible to determine the average structure with a Cl : C ratio of nearly 1 : 2. Thus, the calculated B-Cl/C bond lengths of $1.678(4)$ and $1.689(2) \text{ \AA}$ are too long for pure B-C bonds like in 2,4,6-trimethylborazine (1.52 \AA [33]), and too short for pure B-Cl bonds as found in 2,4,6-trichloroborazine (1.76 \AA [34]) or in $[(Si(CH_3)_3)NCl]_3$ (1.79 \AA [22]). The protons of the boron bonded methyl groups were localized in difference fourier maps during the structure solution, however, due to the mentioned mixed occupation, refinement of these positions was not possible.

Table 1 Crystallographic data of $[(SiCl_3)NB(Cl_n(CH_3)_{1-n})]_3$

Space group	<i>Pnma</i> (No. 62)
<i>a</i> / \AA	10.500(5)
<i>b</i> / \AA	17.646(5)
<i>c</i> / \AA	10.699(5)
$\alpha, \beta, \gamma / ^\circ$	90, 90, 90
Cell volume / \AA^3	1982(1)
Formula units <i>Z</i>	4
Calculated density / g cm^{-3}	1.808(1)
Absorption coefficient / mm^{-1}	1.59
<i>F</i> (000)	1044.5
Index range	$-13 \leq h \leq 12$ $-21 \leq k \leq 21$ $-13 \leq l \leq 13$
$\Theta_{\max} / ^\circ$	52.48
<i>T</i> / K	100
Measured reflections	18247
Independent reflections	2069
<i>R</i> _{int}	0.0295
No. variables	105
GOOF	1.224
$R_1/[F^2 > 2\sigma(F^2)]$	0.0301
<i>R</i> ₁ (all)	0.0360
<i>wR</i> ₂	0.0867
$\Delta\rho_{\max}, \Delta\rho_{\min} / \text{e}\cdot\text{\AA}^{-3}$	0.56, -0.41

Table 2 Selected bond lengths, bond angles and torsion angles of $[(SiCl_3)NB(Cl_n(CH_3)_{1-n})]_3$

Bond length / \AA		Bond angles / $^\circ$	
B1-N1	1.452(3)	N1'-B1-N1	119.2(3)
B2-N1	1.455(3)	B1-N1-B2	118.2(2)
B2-N2	1.455(3)	N1-B2-N2	118.6(2)
B1-Cl1/C1	1.682(4)	B2-N2-B2'	118.4(3)
B2-Cl2/C2	1.691(3)	Si1-N1-B1	120.2(2)
Si1-N1	1.731(2)	Si1-N1-B2	121.5(2)
Si2-N2	1.728(3)	Si2-N2-B2	120.7(1)
Si1-Cl11	2.019(1)	Cl1/C1-B1-N1	120.1(1)
Si1-Cl12	2.016(1)	Cl2/C2-B2-N1	120.4(2)
Si1-Cl13	2.016(1)	Cl2/C2-B2-N2	120.3(1)
Si2-Cl21	2.004(1)	Cl11-Si1-N1	110.8(1)
Si2-Cl22	2.024(2)	Cl12-Si1-N1	112.4(1)
		Cl13-Si1-N1	111.5(1)
		Cl21-Si2-N2	112.1(1)
		Cl22-Si2-N2	111.2(1)
Torsion angles / $^\circ$			
B1-N1-B2-N2	24.0	Cl11-Si1-Cl12	108.3(1)
Cl1/C1-B1-N1-Si1	-29.3	Cl11-Si1-Cl13	105.1(1)
Si1-N1-B2-Cl2/C2	30.3	Cl12-Si1-Cl13	108.4(1)
Cl2/C2-B2-N2-Si2	-29.3	Cl21-Si2-Cl22	109.1(1)
		Cl22'-Si2-Cl22	103.7(1)

Characterization of the polymer derived from $[(\text{SiCl}_3)\text{NB}(\text{Cl}_n(\text{CH}_3)_{1-n})_3]$

Polymerization of the borazine mixture with methylamine produced a solid polymer which is still soluble in hexane and benzene. The amination of the chlorine functions of the silicon and boron atoms has led to a high field shift of the signals in the ^{29}Si and in the ^{11}B NMR. Boron in a trigonal planar BN_3 environment gives a signal at 27.6 ppm and in a BN_2C environment at 38.9 ppm. Depending on the degree of polymerization the signals for the SiN_4 group occur between -37 and -34 ppm which is in the same range as found for the TADB derived polymer (-33.4 ppm) [8]. The protons of the $\text{Si-N}(\text{CH}_3)$ and $\text{B-N}(\text{CH}_3)$ groups have chemical shifts in the range of 2.12 – 2.73 ppm, while a signal at 0.70 ppm can be assigned to B-CH_3 groups. The carbon signals of the methylamine groups arise in the expected range between 26 and 30.6 ppm.

In the FT-IR spectrum (Figure 2) the characteristic vibration of the borazine ring at 1361 cm^{-1} is visible, partly overlapping with the deformation band of the CH_3 groups (1324 cm^{-1}) of the methylamine ($\text{HN}(\text{CH}_3)$) groups, the antisymmetric vibrations of which give bands at 2813, 2895 and 2933 cm^{-1} . The NH bonds generate an antisymmetric stretching band at 3431 cm^{-1} and a deformation band at 1103 cm^{-1} . The vibration at 923 cm^{-1} is caused by SiN bonds and is slightly shifted to higher wave number compared to the borazine derivatives.

The thermal degradation of the polymer was investigated by TG/MS (Figure 4). In accordance to the pyrolysis of other polyborocarbosilazanes [8, 20, 21] the polymer degrades in three stages. Mainly the polycondensation is completed at $450\text{ }^\circ\text{C}$ evolving methylamine ($m/z = 31$), however, also as a first product of fragmentation small amounts of HCN ($m/z = 27$) are cleaved. The major weight loss (23.1 %) occurs between 450 and $650\text{ }^\circ\text{C}$ releasing methane ($m/z = 16$) splitting of from terminal $\text{N}(\text{CH}_3)$ groups. At temperatures above $600\text{ }^\circ\text{C}$ nitrogen and hydrogen is eliminated resulting in a weight loss of 1.7 %. The overall ceramic yield is 61.9 %.

Characterization of the Si/B/N/C ceramic

The $[(\text{SiCl}_3)\text{NB}(\text{Cl}_n(\text{CH}_3)_{1-n})_3]$ derived polymer was pyrolysed at $900\text{ }^\circ\text{C}$ and calcined at $1400\text{ }^\circ\text{C}$ in an argon atmosphere. The as-obtained black Si/B/N/C ceramic is amorphous with respect to X-ray diffraction (Figure 6). The density of the ground substance was found as 1.80 g cm^{-3} . The elemental analysis of the completely dissolved ceramic sample (Table 3) confirms in correspondence with a the composition of the borazine precursor the Si : B ratio of 1 : 1. Carbon was introduced as terminal CH_3 -groups and has entered the final Si/B/N/C ceramic at 11.44 wt.-%. Thus, the overall composition can be approximately reflected by the bulk formula SiBN_3C ($\equiv \text{SiBN}_3\text{C}_{0.9}\text{O}_{0.1}$).

Table 3 Chemical analysis of the Si/B/N/C ceramic

Element	Mass / %	Empirical formulae
Si	30.15	$\text{Si}_{1.0}\text{B}_{1.0}\text{N}_{3.0}\text{C}_{0.9}\text{O}_{0.1}$
B	11.67	
N	45.08	
C	11.44	
O	1.25	

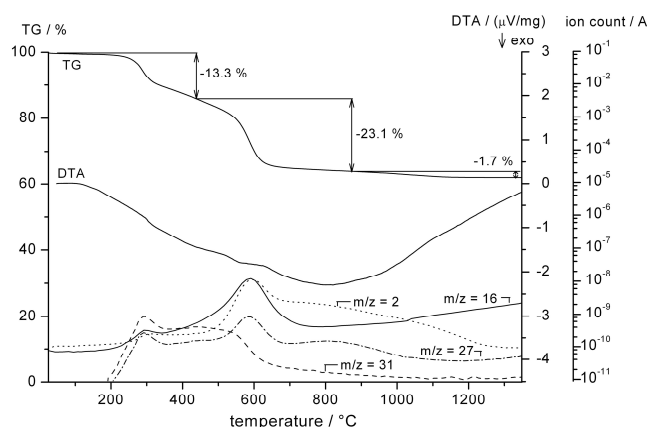


Figure 4 Curves of TG, DTA and ion counts of selected mass to charge ratios assigned to the gaseous species H_2 ($m/z = 2$), CH_4 ($m/z = 16$), HCN ($m/z = 27$), $(\text{CH}_3)\text{NH}_2$ ($m/z = 31$) recorded by simultaneous mass spectroscopy for the pyrolysis of the derived polymer.

The FT-IR absorption bands are very broad due to the presence of many different local topologies (inhomogeneous line broadening) (Figure 2). The vibrations at 1380 cm^{-1} as well as at 793 cm^{-1} are assigned to the antisymmetric stretching mode of the B-N bonds of the borazine ring and indicate the BN heterocycle to be a constitutive building unit of the ceramic. The bands at 978 cm^{-1} and at 485 cm^{-1} can be assigned to the stretching and the deformation modes of Si-N bonds.

With respect to the weight loss, the ceramic is stable up to $1840\text{ }^\circ\text{C}$ (Figure 5). Above $1840\text{ }^\circ\text{C}$, a rapid mass loss is observed and after heating up to $2000\text{ }^\circ\text{C}$ a weight loss of 13 % was recorded. In comparison to some other pre-described Si/B/N/C ceramics $\text{SiB}_{1.44}\text{N}_{2.20}\text{C}_{0.92}\text{O}_{0.21}$ derived from a similar molecular single source precursor $[(\text{SiCl}_3)\text{-NH-BNH}_3]$ containing a borazine ring [36] the ceramic described here shows an improved thermal stability.

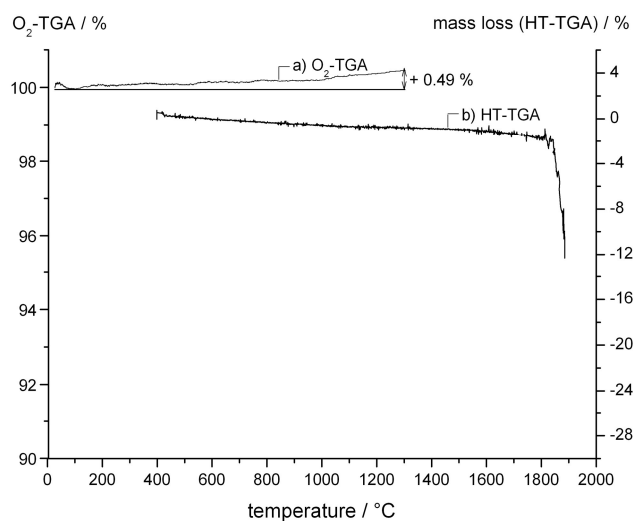


Figure 5 a) TG curve of the derived Si/B/N/C ceramic upon heating up to $1300\text{ }^\circ\text{C}$ in a flow of pure oxygen. b) Mass loss of the ceramic at heating up to $1890\text{ }^\circ\text{C}$ with 10 K min^{-1} in argon flow (first run).

In order to study the crystallization behavior of the ceramic it was heated up to, and annealed at, different temperatures, and investigated ex-situ by XRD (Figure 6). The pattern of the sample annealed at 1600 °C shows only small reflections of silicon carbide indicating a reordering of the network at this temperature. After the thermal treatment at 1800 °C for 3 h the crystallization of the material is significantly advanced showing intense reflections of silicon carbide, boron nitride and silicon. The observation of crystalline silicon as a result of a high temperature treatment is uncommon and occurs only in few other Si/B/N/C ceramics like $\text{SiB}_{1.44}\text{N}_{2.20}\text{C}_{0.92}\text{O}_{0.21}$ [36], derived from a borazine type precursor, and $\text{SiB}_{0.5}\text{N}_{1.5}\text{C}$ [37] obtained from an acyclic molecule. The occurrence of silicon most probably results from thermal decomposition of intermediate silicon nitride under evolution of nitrogen as indicated by the aforementioned abrupt weight loss at 1840 °C. The presence of free carbon in direct contact to silicon nitride can be excluded for thermodynamic reasons: Si_3N_4 (or Si-N units in an amorphous state) would decompose at lower temperatures and would form silicon carbide [38–40]. Furthermore, it can be suggested that the borazine rings are connected by SiN_4 units preventing the formation of boron nitride phases at $T < 1800$ °C. The thermal decomposition of these cross-linking units leads to the crystallization of BN at $T > 1800$ °C.

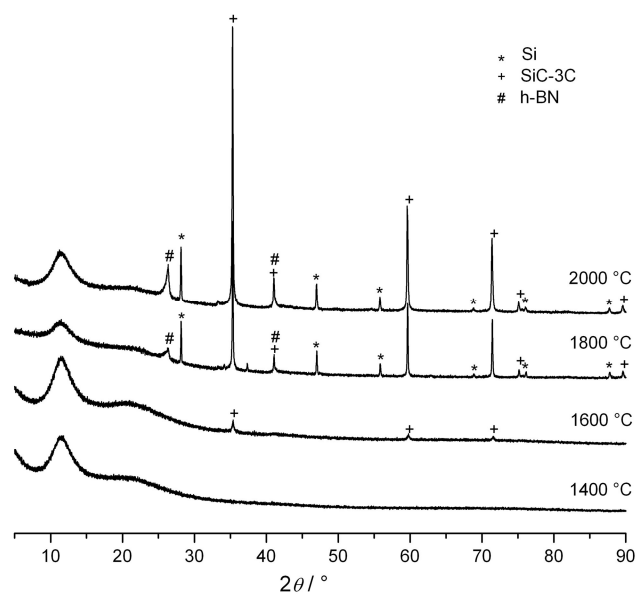


Figure 6 XRD pattern of the derived Si/B/N/C ceramic after the pyrolysis at 1400 (3h) and the thermal treatment at 1600 (3h), 1800 (3h) and 2000 °C (no dwell time).

The investigation of the oxidation behaviour of the ceramic, which is important for its application under atmospheric conditions, was performed between room temperature and 1300 °C in a flow of pure oxygen (Figure 5). During the heating only a slight increase in weight of 0.49 % up to 1300 °C is observable. This effect is credited to the formation of a passivating surface double layer which protects the ceramic against further oxidation [6]. The in comparison to $\text{SiB}_{1.44}\text{N}_{2.20}\text{C}_{0.92}\text{O}_{0.21}$ [36] improved oxidation stability, which showed a mass loss of 6.5 % at 700 °C while releasing carbon dioxide, is indicative for the absence of carbonaceous regions within the network. In combination

with the featureless DTA track, decomposition or far-reaching oxidation processes inside the ceramic can be excluded.

Conclusions

New borazine derivatives $[(\text{SiCl}_3)\text{NB}(\text{Cl}_n(\text{CH}_3)_{1-n})_3]$ with nitrogen bonded silyl groups have been prepared and characterized. Following the polymer route, the borazine derivatives were cross-linked with methylamine. The resulting polymer was pyrolyzed, following a special temperature schedule up to 1400 °C, to an amorphous ceramic material with the approximate elemental composition of SiBN_3C . Above 1600 °C it starts to decompose forming crystalline silicon, silicon carbide and boron nitride phases detectable after annealing at 1800 °C. Compared to the ceramic derived from the other known comparable precursor with a borazine ring, SiCl_3 groups and nitrogen as linkage between boron and silicon [36], the present one has shown an improved thermal stability up to 1800 °C as well as oxidation resistance of up to 1300 °C. In comparison to other pre-described Si/B/N/C ceramics the properties like high temperature stability and crystallisation durability could not be enhanced, however. Furthermore, the introduction of borazine ring structures favours the formation of crystalline boron nitride phases, above the decomposition temperature of the ceramic.

Experimental Section

General procedures

All reactions were performed under an inert argon atmosphere in carefully dried glassware and solvents. HMDS (Fluka) was distilled over molecular sieves (Merck), SiCl_4 (VWR), and $(\text{CH}_3)_2\text{SiCl}_2$ (Sigma Aldrich) were distilled over magnesia turnings (Riedel-de Haën). Hexane, m-xylene (Acros Organics) and undecane (Fisher Scientific) were dried over sodium/benzophenone (Merck). Butyl lithium (2.5 M in hexane, Sigma Aldrich), BCl_3 (purity 99.9, 3.0, WESTFALEN) and $(\text{CH}_3)\text{NH}_2$ (purity 99.5, 2.5, Gerling Holz und Co) were used without further purification.

Characterization techniques

NMR spectroscopic measurements in C_6D_6 were carried out at a spectrometer AVANCE DPX-300 SB (Bruker) equipped with a 300 MHz magnet ($B_0 = 7.05$ T) working at 300.13 MHz (^1H NMR), 75.46 MHz (^{13}C NMR), 96.29 MHz (^{11}B NMR), or 59.63 MHz (^{29}Si NMR). IR spectra were recorded on a Bruker IFS 113v FT-IR spectrometer in the range between 400 and 4000 cm^{-1} using KBr pellets for solid materials or KBr windows for films of liquid samples. Mass spectra were obtained using a mass spectrometer GCMS-QP2010 Plus (Shimadzu) with electron impact ionization (60 eV).

The thermal degradation of the polymer was examined using simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TG) in a Netzsch STA409 (heating rate 5 $\text{K}\cdot\text{min}^{-1}$, argon flow) equipped with a Balzer QMS421 quadrupole mass spectrometer. The high temperature TGA was performed in a Bähr STA501 (10 $\text{K}\cdot\text{min}^{-1}$, argon-flow) in a graphite crucible. To analyze the composition of the obtained ceramic material the contents of nitrogen and oxygen were

simultaneously determined in a Leco TC-436 hot gas extraction analyzer, while carbon was measured in a Leo C-200 hot gas extraction analyzer. Silicon and boron were quantified in a Varian Vista-Pro ICP-OES spectrometer after solving the ceramic sample in a mixture of HF-HNO₃ [44]. The density of the ceramic was investigated by helium pycnometry using an AccuPyc II 1340 gas pycnometer (Micromeritics). Powder diffraction patterns were recorded using a STOE Stadi-P diffractometer in transmission mode with Debye-Scherrer geometry (germanium-monochromated Cu K_{α1}, position sensitive detector (PSD)).

Data collection (100 K) for single crystal structure analysis was performed on a Smart APEX II three circle single crystal diffractometer (Bruker) equipped with a CCD-detector using Mo-K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The data reduction were done with the Bruker Suite software package [41], and the semi-empirical correction of the intensities for absorption effects was carried out using the program SADABS [42]. The structure was solved by direct methods. For the structure solution as well as for the refinement the SHELXTL software package [43] was used. For [(SiCl₃)NB(Cl_n(CH₃)_{1-n})₃], the CCDC No. 769047 contains the supplementary crystallographic data, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis

1,1,1-trichloro-3,3,3-trimethylidisilazane (TTDS) was synthesized by converting hexamethyldisilazane (HMDS) with silicontetrachloride (SiCl₄) in accordance to a slightly modified procedure [1] reported by Nöth [45]. 1-Monochloro-1,1,3,3,3-pentamethylidisilazane (MPDS) was obtained by the reaction of HMDS with dichlorodimethylsilane Cl₂Si(CH₃)₂ according to the method of Müller et al. [10].

Dichloroboryl-(trichlorosilyl)-(trimethylsilyl)-amine was prepared by an adaptation of procedures described by Wannagat [46] and Neilson [47]. 23.5 g TTDS (0.105 mol) is dissolved in 200 ml hexane and cooled to -78 °C in a dry ice / isopropanol bath. Subsequently, 42.3 ml of a 2.5 M BuLi / hexane solution is dropped under stirring. The reaction mixture is warmed to 0 °C in an ice bath holding this temperature for 1 h followed by cooling to -78 °C. 8.6 ml of BCl₃ are condensed to the solution which is allowed to warm to room temperature over night. By using a G3 frit the formed lithium chloride is filtrated and washed with 20 ml hexane. After removing the solvent in slight vacuum, a fractionated distillation of the residue at 32 °C/5.5·10⁻³ mbar yielded 24 g (80 %) of the product as a colorless liquid. NMR in C₆D₆: ¹H NMR: $\delta = 0.29$ ppm. ¹³C NMR: $\delta = 2.69$ ppm. ¹¹B NMR: $\delta = 40.1$ ppm. ²⁹Si NMR: $\delta = -26.2$ ppm (SiCl₃), 16.3 ppm (s, Si(CH₃)₃). IR (film): $\tilde{\nu} = 2960$ (vw), 2905 (vw), 1420 (vw), 1275 (m), 1259 (st), 1229 (vst), 980 (m), 956 (vst), 871 (m), 846 (st), 770 (s), 592 (st), 532 (s), 505 (m) cm⁻¹.

For synthesizing **dichloroboryl-(chlorodimethylsilyl)-(trimethylsilyl)-amine (CBTA)**, the procedure described above was used converting MPDS instead of TTDS. The colorless product is distilled at 32 °C / 5·10⁻³ mbar, yield 19.2 g (74 %). NMR in C₆D₆: ¹H NMR: $\delta = 0.31$ (s, 9H, Si(CH₃)₃), 0.51 (s, 6H, Si(CH₃)₂Cl) ppm. ¹³C NMR: $\delta = 3.42$ (Si(CH₃)₃), 6.66 (Si(CH₃)Cl) ppm. ¹¹B NMR: $\delta = 37.4$ ppm. ²⁹Si NMR: $\delta = 12.7$ (Si(CH₃)₃), 17.3 ppm (s, Si(CH₃)₂Cl). IR (film): 2960 m, 2905 (w), 1409 (m), 1308 (st), 1276 (vst), 1260 (vst), 959 (st), 959 (st), 937 (vst), 869

(vst), 854 (vst), 801 (st), 768 (m), 664 (w), 623 (w), 534 (m), 490 (w) cm⁻¹.

Borazine derivatives [(SiCl₃)NB(Cl_n(CH₃)_{1-n})₃]

20.8 g of dichloroboryl-(trichlorosilyl)-(trimethylsilyl)-amine is heated in 120 ml boiling undecane at 196 °C for 7 days. After removing the side-products and the solvent at 80 °C / 18 mbar the solid residue is dissolved in 15 ml hexane. By cooling this solution to 7 °C pale yellow crystals could be obtained which were isolated, dried at room temperature / 10⁻³ mbar and sublimed at 60 °C / 10⁻³ mbar yielding 6.3 g (50 %) of the colorless borazine derivative. NMR in C₆D₆: ¹H NMR: $\delta = 0.91$ ppm (s, B(CH₃)) 0.98 (s, B(CH₃)). ¹³C NMR: not observed B(CH₃). ¹¹B NMR: $\delta = 33.2$ ppm (BCl), 43.5 ppm (B(CH₃)). ²⁹Si NMR: $\delta = -21.3$ ppm (t, ¹J_{Si,N} = 30 Hz, SiCl₃). IR (KBr plates): 2962 (vw), 1446 (w), 1336 (vs), 1302 (vs), 1279 (vs), 1212 (w), 1112 (w), 1074 (w), 910 (s), 842 (w), 720 (m), 703 (m), 678 (w), 635 (w), 610 (vs), 588 (vs), 495 (m), 470 (s), 450 (w) cm⁻¹.

Chloromethylboryl-bis(chlorodimethylsilyl)amine (SiCl(CH₃)₂)₂NBCl(CH₃) (CBCA)

6 g (0.023 mol) dichloroboryl-(chlorodimethylsilyl)-(trimethylsilyl)-amine (CBTA) is dissolved in 150 ml m-xylene and heated to 140 °C for 2 d. After removing the solvent at 58 °C / 1·10⁻² mbar yielding 3.1 g (88 %). NMR in C₆D₆: ¹H NMR: $\delta = 0.53$ (s, 12 H, Si(CH₃)₂Cl), 0.87 (s, 3 H, BCl(CH₃)) ppm. ¹³C NMR: $\delta = 6.78$ (Si(CH₃)₂Cl) ppm, BCl(CH₃) not observed. ¹¹B NMR: $\delta = 51.0$ (BCl(CH₃)) ppm. ²⁹Si NMR: $\delta = 15.9$ ppm (Si(CH₃)₂Cl).

Preparation of the pre-ceramic polymer

1.5 g (0.0026 mol) of the borazine derivatives dissolved in 50 ml hexane is dropped slowly to a solution of 2 ml (CH₃)NH₂ condensed into 30 ml hexane at -78 °C. After warming the resulting reaction mixture to room temperature over night the formed methylamine hydrochloride precipitate is removed by filtration and washed with 50 ml hexane. From the combined filtrates the solvent is stripped in vacuum leaving the polymer as a colorless solid examined by NMR and IR. Some polymer is annealed at 230 °C / 24 h for further condensation and investigated by TG / MS.

Pyrolysis and calcination of the pre-ceramic polymer

The polymer is transferred to an inert corundum crucible, which is positioned in a quartz tube placed in a horizontal furnace. The sample is heated up to 300 °C at a rate of 100 K·h⁻¹, maintained at this temperature for 3 h. Then the temperature is raised to 900 °C with 100 K·h⁻¹ followed by a dwell time of 3 h. The pyrolyzed sample is calcined for 3 h at 1400 °C. All steps are carried out under argon flow.

Acknowledgement

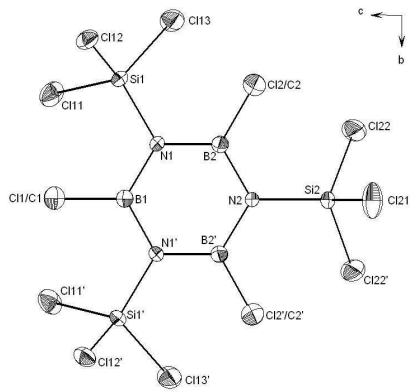
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[1] O. Wagner, *Diploma thesis*, Universität Bonn, Germany, 1991.

- 1
2 [2] M. Jansen, H.-P. Baldus, O. Wagner, EP0502399A2, **1992**.
3 [3] H.-P. Baldus, M. Jansen, O. Wagner, *Key Eng. Mater.*, **1994**,
4 89-91, 75.
5 [4] R. Riedel, A. Kienzle, W. Dressler, L. Ruwisch, J. Bill, F.
6 Aldinger, *Nature*, **1996**, 382, 796.
7 [5] H.-P. Baldus, M. Jansen, *Angew. Chem.*, **1997**, 109, 338.
8 [6] P. Baldus, M. Jansen, D. Sporn, *Science*, **1999**, 285, 699.
9 [7] M. Jansen, B. Jäschke, T. Jäschke, *Structure and Bonding*,
10 **2002**, 101, 137.
11 [8] M. Jansen, M. Kroschel, *Z. Anorg. Allg. Chem.*, **2000**, 626,
12 1634.
13 [9] M. Jansen, U.Müller, J. Clade, WO002002022624 (A1),
14 **2002**.
15 [10] U. Müller, M. Weinmann, M. Jansen, *J. Mater. Chem.*, **2008**,
16 18, 3671.
17 [11] M. Kroschel, M. Jansen, WO002002022522 (A2), **2002**.
18 [12] M. Weinmann, M. Kroschel, T. Jäschke, J. Nuss, M. Jansen,
19 G. Kolios, A. Morillo, C. Tellaiche, U. Nieken, *J. Mater.*
20 *Chem.*, **2008**, 18, 1810.
21 [13] M. Weinmann, M. Jansen, WO002009124725A1, **2009**.
22 [14] T. Jäschke, M. Jansen, *C. R. Chimie*, **2004**, 7, 471.
23 [15] T. Jäschke, M. Jansen, *J. Eur. Ceram. Soc.*, **2005**, 25, 211.
24 [16] H. Jüngermann, M. Jansen, *Mater. Res. Innovations*, **1999**, 2,
25 200.
26 [17] Y.H. Schlleier, A. Verhoeven, M. Jansen, *Angew. Chem. Int.*
27 *Ed.*, **2008**, 47, 3600.
28 [18] L. van Wüllen, U. Müller, M. Jansen, *Angew. Chem.*, **2000**,
29 112, 2574; L. van Wüllen, U. Müller, M. Jansen, *Angew.*
30 *Chem. Int. Ed. Engl.*, **2000**, 39, 2519; L. van Wüllen, M.
31 Jansen, *Chem. Mater.*, **2000**, 12, 2347; L. van Wüllen, M.
32 Jansen, *J. Mater. Chem.*, **2001**, 11, 223;
33 [19] J. Haberecht, F. Krumeich, H. Grützmacher, R. Nesper,
34 *Chem. Mater.*, **2004**, 16, 418.
35 [20] J. Haberecht, R. Nesper, H. Grützmacher, *Chem. Mater.*,
36 **2005**, 17, 2340.
37 [21] T. Jäschke, M. Jansen, *J. Mater. Chem.*, **2006**, 16, 2792.
38 [22] B. Anand, H. Nöth, H. Schwenk-Kircher, A. Troll, *Eur. J.*
39 *Inorg. Chem.*, **2008**, 3186.
40 [23] W. Einholz, W. Gollinger, W. Haubold, *Z. Naturforsch.*,
41 **1990**, 45b, 25.
42 [24] W. Haubold, U. Kraatz, *Z. Anorg. Allg. Chem.*, **1976**, 421,
43 105.
44 [25] K. Barlos, H. Nöth, *Chem. Ber.*, **1977**, 110, 3460.
45 [26] K. Barlos, H. Nöth, *Chem. Ber.*, **1977**, 110, 2790.
46 [27] T. Habereeder, H. Nöth, *Z. Anorg. Allg. Chem.*, **2001**, 627,
47 1003.
48 [28] T. Chivers, C. Fedorchuk, M. Parvez, *Acta Cryst. C*, **2005**, 61,
49 47.
50 [29] G. Huttner, B. Krieg, *Chem. Ber.*, **1972**, 105, 3437.
51 [30] B. Gemünd, B. Günther, J. Knizek, H. Nöth, *Z. Naturforsch.*,
52 **2008**, 63b, 23.
53 [31] T. Jäschke, M. Jansen, *Z. Anorg. Allg. Chem.*, **2004**, 630, 239.
54 [32] J. Haberecht, A. Krummland, F. Breher, B. Gebhardt, H.
55 Rügger, R. Nesper, H. Grützmacher, *Dalt. Trans.*, **2003**,
56 2126.
57 [33] K. Anzenhofer, *Mol. Phys.*, **1966**, 11, 494.
58 [34] D.L. Coursen, J.L. Hoard, *J. Am. Chem. Soc.*, **1952**, 74, 1742.
59 [35] R. Boese, A.H. Maulitz, P. Stellberg, *Chem. Ber.*, **1994**, 127,
60 1887.
[36] A. Epple, *PhD Thesis*, Max-Planck-Institut für
Festkörperforschung, Stuttgart, Germany, **2006**.
[37] M. Kroschel, *PhD Thesis*, Universität Bonn, Germany, **2001**.
[38] A. Kato, H. Mizumoto, Y. Fukushige, *Ceram. Int.*, **1984**, 10,
37.
[39] H. Jüngermann, M. Jansen, *Mat.-wiss. u. Werkstofftech.*,
1998, 29, 573.
[40] M. Weinmann, J. Schuhmacher, H. Kummer, S. Prinz, J.Q.
Peng, H.J. Seifert, M. Christ, K. Müller, J. Bill, F. Aldinger,
Chem. Mater., **2000**, 12, 623.
[41] Bruker Suit, Version 2008/3, Bruker AXS Inc., Madison, WI,
USA **2008**.
[42] Sheldrick, G.M.: SADABS – Bruker AXS area detector
scaling and absorption, version 2008/1, University of
Göttingen, Germany **2008**.
[43] Sheldrick, G.M. *Acta Crystallogr. Sect. A*, **2008**, 64, 112.
[44] S. Mann, D. Geilenberg, J.A.C. Broekaert, M. Jansen, *J. Anal.*
Atomic Spect., **1997**, 12, 975.
[45] J. P. Mooser, H. Nöth, W. Tinhof, *Z. Naturforsch.*, **1974**, 29b,
166.
[46] P. Geymayer, E.G. Rochow, U. Wannagat, *Angew. Chem.*,
Int. Ed. Engl., **1964**, 3, 633.
[47] B.-L. Li, M.A. Goodman, R.H. Neilson, *Inorg. Chem.*, **1984**,
23, 1368.

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Borazine based molecular single source precursors for Si/B/N/C ceramics