

Improved durability of Si/B/N/C random inorganic networks

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Abstract

The inherent high temperature durability as well as the hardness of random inorganic networks composed of Si, B, N and C, can be raised through the incorporation of rigid structural elements (e.g. borazine rings) as well as through an increase of the carbon content. This has been shown by comparison of the high temperature durabilities and micromechanical properties of newly synthesized Si/B/N/C ceramics derived from different acyclic and cyclic single source precursors. Crosslinking of these specially designed monomers with methylamine provides highly homogeneous preceramic polymers, in which the predetermined structural features of the molecular precursors are embedded. Subsequent pyrolysis and calcination up to 1500 °C converts the polymers into all-inorganic amorphous silicon boron carbonitrides. Depending on the constitution of the precursors, the as-obtained materials exhibit a combination of a high carbon content together with borazine rings embedded into the covalent network. Comparing the high temperature stability, hardness and stiffness of the synthesized ceramics, the best performance is achieved when carbon rich borazine derivatives are employed as single source precursors. Thus, the high temperature durability can be raised up to at least 2000 °C, and, at the same time, the microhardness and elastic modulus is maximized up to 14.5 and 127 GPa, respectively. The new materials have been characterized by IR spectroscopy, elemental analysis, XRD, SEM, DTA/TG, and by nanoindentation. © 2004 Elsevier Ltd. All rights reserved.

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1. Introduction

The outstanding thermal, chemical and mechanical properties of random inorganic networks based on the quaternary system Si/B/N/C have caused growing interest in such high performance materials in recent years.¹ Especially the superior high temperature durability even under oxidizing conditions, combined with low densities make these ceramics highly attractive for applications under extreme conditions like in heat engines (in particular turbines), as well as in aviation and aerospace.² In recent years, much work has been done in order to further enhance the advantageous intrinsic properties of Si/B/N/C ceramics, and also to understand the relationships between the structure of the amorphous covalent networks and their material properties.³ Clearly, there exist many open questions concerning this rather young class of materials, stimulating an ongoing development of these multinary non-oxide ceramics. Unlike multinary oxide ceramics, the preparation of silicon boron carbonitrides can-

not proceed via conventional solid-state reactions, or through melting processes, starting from the pure elements or the respective binary compounds. Due to incongruent melting behavior of the nitrides and carbides of silicon and boron, and since these cationic elements exhibit very low self-diffusion coefficients^{4,5} the only feasible approach known so far is the 'polymer route'.^{6–8} Following this reaction path, one or more metalorganic monomers are polymerized (usually by polycondensation reactions) to yield preceramic polymers which are then pyrolyzed at high temperatures until a pure inorganic solid remains.

As a crucial point, the performance of these multinary non-oxide ceramics depends strongly on the homogeneity of the preceramic polymer. Spatial inhomogeneities at the polymer stage have to be avoided, since they induce phase separation and decomposition of the multinary ceramic into its border phases during pyrolysis or thermal load. Thus, cocondensation of different molecular precursors is unfavorable, because different velocities in the substitution reactions of the individual molecular species usually lead to clustering of one cationic species. Instead, highly homogeneous preceramic polymers are obtained using specially designed

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monomers, so-called ‘single source precursors’, which already contain the electropositive elements in the ratio desired for the final ceramic linked together via a carbon or nitrogen atom.⁹ As both cations are fixed to the bridging group by strong covalent bonds the entire backbone of the precursor survives the crosslinking procedure, leading to a preceramic polymer with a homogeneous distribution of the constituting elements on an atomic scale.¹⁰ As can be seen from the thermal stabilities of Si/B/N/C materials, the incorporation of carbon into the random network increases the thermal durability significantly.^{11,12} It is reasonable that an additional improvement of the high temperature stability can be achieved by further increasing the carbon content of the silicon boron carbonitrides. However, it should also be considered that a higher amount of carbon incorporated affects the good intrinsic oxidation resistance of Si/B/N/C ceramics, thus lowering their potential for applications at elevated temperatures under atmospheric conditions.

As an option, one could try to reinforce and stabilize the amorphous network additionally through the incorporation of rigid structural elements, which could act as inhibitors suppressing conformational changes inside the random network. As a crucible precondition, such building units have to be thermally durable, because they must not decompose at elevated temperatures for which the material is designed. An atom group which fulfills these requirements of rigidity and stability nearly perfectly is the six-membered planar borazine ring, being extremely inflexible and stiff due to strong p_{π} – p_{π} interactions between boron and nitrogen. By polymerizing suitably functionalized borazine derivatives to serving as single source precursors, it should be possible to incorporate such units into the preceramic polymer, and thus into the final ceramic.

In this contribution we present the synthesis and characterization of new amorphous ceramics in the quaternary system Si/B/N/C. Starting from acyclic and cyclic single source precursors, random inorganic networks are prepared with combinations of different carbon contents and borazine rings incorporated.

2. Experimental

2.1. General procedures

All reactions were carried out under inert atmosphere (argon) in rigorously dried reaction apparatus and solvents. Hexane was distilled from CaH_2 (Merck). Commercially available methylamine (Messer Griesheim) was used without further purification.

2.2. Characterization techniques

IR spectra were recorded between 400 and 4000 cm^{-1} on a Bruker IFS 113v FT-IR spectrometer, using KBr pellets.

Scanning Electron Microscopy. SEM pictures of the ceramics were obtained from a Philips XL30 TMP scanning electron microscope.

Thermal degradation of the preceramic polymers has been studied by means of simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) in a Netzsch STA 409 (heating rate 10 K min^{-1} , argon flow) equipped with a Balzers QMS421 quadrupole mass spectrometer. The oxidation behavior of the synthesized ceramics was checked by heating the samples in a flow of pure oxygen up to $1300\text{ }^{\circ}\text{C}$ at a rate of 10 K min^{-1} .

Quantitative analyses of nitrogen and oxygen have been carried out simultaneously in a Leco TC-436 hot gas extraction analyzer, whereas carbon was measured in a Leco C-200 hot gas extraction analyzer. Silicon and boron were quantified by means of ICP-OES in an Arl 3580B spectrometer after digestion of the ceramic samples using a mixture of $\text{HF}/\text{HNO}_3/\text{HCl}$.

The macroscopic density of the as-obtained ceramic material was measured using an automatic Micromeritics AccuPyc 1330 helium pycnometer.

Powder X-ray diffraction patterns were recorded on a STOE Stadi-P diffractometer in transmission mode with Debye-Scherrer geometry, with germanium-monochromated $\text{Cu K}\alpha$ radiation. The ceramic powder samples were placed in a glass capillary ($\varnothing 0.5\text{ mm}$) and diffraction patterns were collected between 4° and 76° in 2θ using a position sensitive detector (PSD).

The microhardness and elastic modulus of the ceramic powders were measured using the MTS Nano Indenter XP with a Berkovich triangular pyramid diamond indenter tip. Eleven to twelve indentations per sample were carried out, distributed on several grains, depending on the grain size. At a constant deformation rate of 0.05 s^{-1} and a penetration depth of up to 500 nm the load applied to the sample was recorded as a function of displacement. The powder samples were embedded in epoxy resin and then polished using fine diamond paste. The as-obtained data was statistically analyzed using the computer program ‘Analyst’.

2.3. Synthesis of the precursor molecules

The acyclic single source precursors $\text{Cl}_3\text{Si-CH}_2\text{-BCl}_2$ (TSDM) and $\text{Cl}_2(\text{CH}_3)\text{Si-CH}_2\text{-BCl}_2$ (DSDM) were synthesized according to a recently published procedure.¹³ By reacting these two molecules with hexamethyldisilazane, the new precursors $[\text{B}\{\text{CH}_2(\text{SiCl}_3)\}\text{NH}]_3$ (TSMB) and $[\text{B}\{\text{CH}_2(\text{SiCl}_2\text{CH}_3)\}\text{NH}]_3$ (DSMB) were obtained, respectively.¹⁴

2.4. Preparation of the preceramic polymers

A solution of 13.9 g (61 mmol) TSDM or 11.7 g (56 mmol) DSDM or 15.9 g (30 mmol) TSMB or 16.3 g (35 mmol) DSMB in 150 ml hexane is added dropwise to a solution of 100 ml methylamine (69.4 g , 2.234 mol) in 150 ml hex-

ane at -78°C . The stirred mixture is allowed to reach room temperature, whereupon excessive methylamine evaporates and methylamine hydrochloride precipitates. After filtration of the accumulated ammonium salt the residue is washed two times with 50 ml hexane. The solvent is removed from the filtrate whereupon the respective polymer remains as a viscous colorless liquid, which is further annealed at 80°C for 24 h for solidification.

2.5. Pyrolysis and calcination of the preceramic polymers

The polymers are filled into inerted boron nitride crucibles, which are then placed in a quartz tube. Under slightly flowing argon, the samples are heated in a horizontal furnace up to 300°C at a rate of 100 K h^{-1} followed by a dwell of 3 h to complete crosslinking of the polymers. Subsequently, the temperature is raised to 900°C at 100 K h^{-1} and maintained for another 3 h. Finally, the pyrolyzed samples are heated up to 1500°C at 300 K h^{-1} in alumina crucibles under argon flow and are calcinated at this temperature for another 3 h.

3. Results and discussion

3.1. Design of the single source precursors

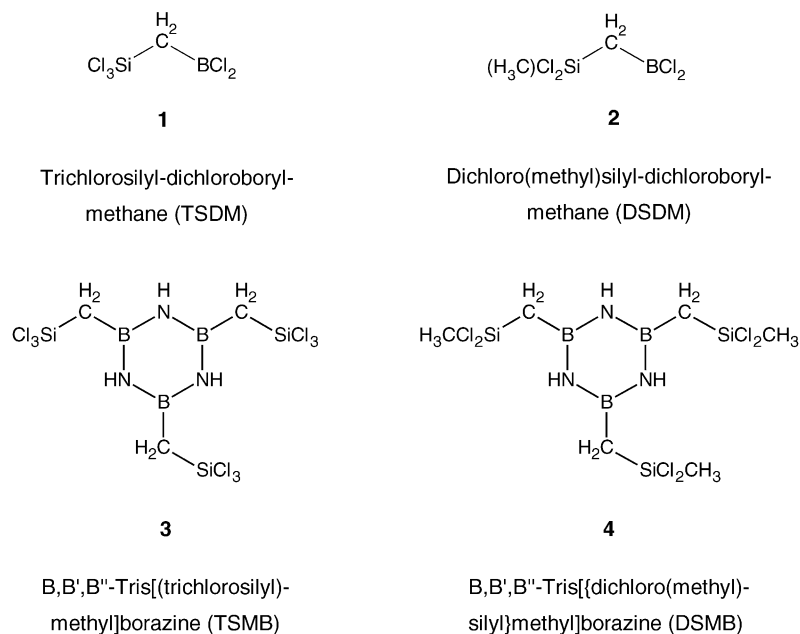
The molecules depicted in Scheme 1 allow for the preparation of Si/B/N/C ceramics with different carbon contents, alternatively combined with borazine rings. To enable crosslinking of these precursors, e.g. with methylamine, the remaining bonding sites of silicon and boron are saturated with chlorine atoms. As a special feature, the cationic ele-

ments boron and silicon are interconnected via a methylene group. Thus, after crosslinking of these precursors, carbon is integrated via *two* covalent bonds into the constituting network instead of only one bond which would be the case when carbon is introduced through a methyl group. Consequently, carbon should be incorporated very efficiently into the pre-ceramic polymer leading in turn to carbon rich compositions of the final ceramic material. Unlike TSDM and TSMB, the precursor molecules DSDM and DSMB exhibit an additional methyl group attached to silicon. This feature permits not only a further increase of the carbon content, but also offers an opportunity for tuning the rheological properties of the polymer, due to the lower number of chlorine functions in DSDM available for polycondensation.

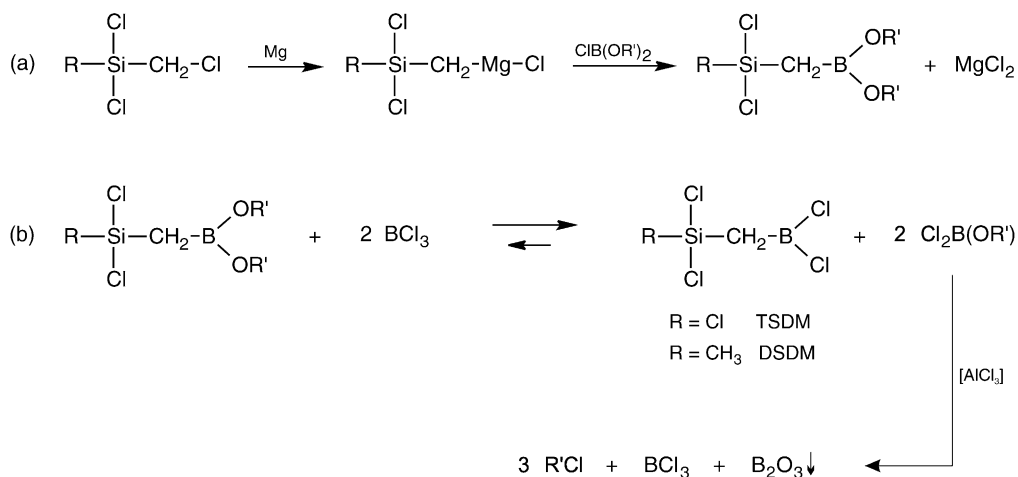
All four precursor molecules contain boron and silicon in the ratio of 1:1. The borazine derivatives TSMB and DSMB are derived from their acyclic counterparts TSDM and DSDM, respectively. The only difference between the acyclic precursors on the one hand, and TSMB and DSMB on the other hand is the fact that the boron sites of the latter are already ‘interconnected’ by nitrogen. Due to their similar connectivities, the molecules pictured in Scheme 1 can be regarded as a small ‘precursor-family’, facilitating the detection of relationships between precursor structure and the derived ceramic.

3.2. Synthesis concept for the molecular precursors

A feasible reaction path for the selective syntheses of the precursors TSDM and DSDM is a metathesis reaction between a suitable organometallic silane and a boron halide (Scheme 2). Although the involved organometallic species $\text{RCl}_2\text{Si}-\text{CH}_2-\text{MgCl}$ tend to self-condensation,¹⁵ this un-



Scheme 1. Cyclic and acyclic single source precursors for the preparation of Si/B/N/C ceramics via the polymer route.



Scheme 2. Reaction path for the preparation of the acyclic single source precursors TSDM and DSDM.

desired side reaction can be suppressed by proper choice of the reaction conditions (dilution principle, low reaction temperature).¹³ The second reaction step shown in Scheme 2b is necessary, because the strong Lewis acid trichloroborane cannot be employed directly for the reaction with the Grignard compound since it reacts readily with the mandatory ether solvent.¹⁶ As a consequence, one has to perform a third reaction step in which the intermediate organoborane dialkylester is converted into the final target molecule (Scheme 2c).

Synthesis of the cyclic single source precursors TSMB and DSMB is much easier, since both molecules are derived from their acyclic counterparts TSDM and DSDM. Thus, by reacting the latter with hexamethyldisilazane the corresponding borazine derivatives form in an almost quantitative yield (Scheme 3).

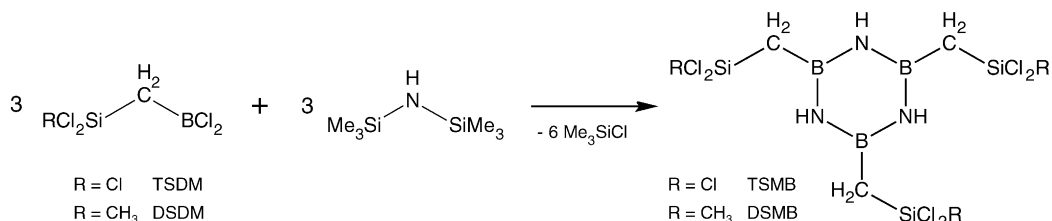
3.3. Preceramic polymers

The single source precursors TSDM, DSDM, TSMB and DSMB are polymerized with methylamine rather than ammonia, thus taking advantage of two important features. Firstly, due to the methyl group present in methylamine, the carbon content, whose significance for the final silicon boron carbonitride has already been discussed in the introduction, is further increased. Secondly, the separation of the polyborocarbosilazane from precipitated methylammonium chlo-

ride, which forms during the polymerization process due to dehydrohalogenation reactions, is facilitated. Since the degree of crosslinking is lower with methylamine than with ammonia the polymer remains soluble in organic solvents (e.g. hexane) and can be simply filtered off from the hydrochloride. After removal of the solvent, the polymers usually remain as a colorless viscous liquid which can be solidified by further thermal treatment.

3.4. Pyrolytic conversion of the preceramic polymers

The pyrolytic conversion of the polymers into the amorphous ceramics was monitored by differential thermal analysis combined with thermogravimetric analysis and mass spectrometry (DTA/TG/MS). Since the measured DTA/TG curves of the investigated polymers are rather similar, their thermal degradation will be discussed together considering as example the TSDM polymer. As can be seen from Fig. 1 the pyrolysis proceeds in two well resolved stages, as had previously been observed during the pyrolytic conversion of other polyborocarbosilazanes [17]. In a first step, between 200 and 450 °C the polycondensation is completed via transamination reactions, accompanied by methylamine elimination. The mass losses at this stage (Table 1) vary between 7.1% and 18.2% depending primarily on the degree of crosslinking of the respective polymer. From 500 to 650 °C with a maximum at about 600 °C, the second step of the thermal



Scheme 3. Synthesis of the cyclic single source precursors TSMB and DSMB for the preparation Si/B/N/C ceramics with incorporated borazine rings.

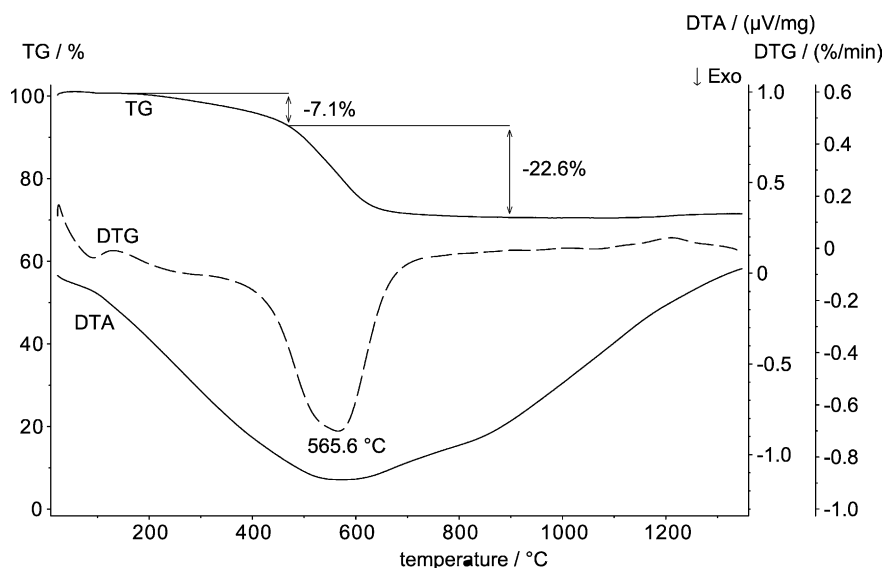


Fig. 1. DTA/TG curves for the pyrolytic conversion of the TSDM polymer.

degradation proceeds, being characterized by the evolution of mainly methane originating from terminal methyl groups (N-CH_3 , Si-CH_3).

The higher mass loss of the DSDM and the DSMB polymer at this stage (the real ‘pyrolysis’ step), is caused by their higher total number of methyl groups which partly evolve as methane at this temperature. While the polymers derived from TSDM and TSMB only contain methyl groups originating from the cross linking reagent methylamine, the DSDM and the DSMB polymer both exhibit additional Si-CH_3 groups. Thus, the ceramic yields are best for the TSDM and TSMB ceramic amounting to 70.3% and 70.4%, respectively. A remarkable high ceramic yield of 94% was recently reported by Nesper and co-workers,¹⁸ who have employed borazine derivatives with vinyl groups for an efficient preparation of Si/B/N/C ceramics. It should be noticed, that the numeric value of a given ceramic yield always depends on the degree of crosslinking of the corresponding preceramic polymer. Since reference points for an exact calculation of the mass balance are not defined uniformly in literature, a straight comparison between ceramic yields of different polymers cannot be accomplished properly.

Table 1
Mass losses of the investigated preceramic polymers during thermal degradation up to 1350 °C

Preceramic polymer derived from	Mass loss (wt.%)		Ceramic yield (%)
	Stage 1 (200–450 °C)	Stage 2 (500–650 °C)	
TSDM	7.1	22.6	70.3
DSDM	18.1	34.4	47.5
DSMB	14.6	15.0	70.4
TSMB	18.2	22.1	59.7

3.5. Si/B/N/C ceramics

Pyrolysis of the preceramic polymers derived from the precursors TSDM, DSDM, TSMB and DSMB yield black grains of the corresponding Si/B/N/C ceramics. As can be seen from the scanning electron micrographs in Fig. 2, no porosity is noticeable. The surface and morphology of the ceramic grains is irregular with sharp edges characteristic for non-crystalline solids. The XRD patterns shown in Fig. 3 confirm, that the as-obtained materials are X-ray amorphous after pyrolysis and calcination at 1500 °C.

From the infrared spectra of the newly synthesized Si/B/N/C ceramics (Fig. 4) it can be seen, that the borazine rings introduced via the single source precursors TSMB and DSMB are incorporated into the final ceramics. This is clearly indicated by the strong and characteristic band at 1426 cm^{-1} , typical for the antisymmetric stretching mode of borazine rings confirming the presence of these cyclic units in the random network after the polymer-to-ceramic conversion. In contrast, the IR spectra of the Si/B/N/C ceramics derived from the acyclic precursors TSDM and DSDM exhibit a much weaker and broad absorption between 1300 and 1500 cm^{-1} pointing out common B–N stretching vibrations. Although the presence of few borazine rings cannot be excluded entirely, it can be stated that no noticeable amount of these units is existent in these ceramics. All of the spectra have in common broad bands typical for the structural increments Si–N, Si–C (both 700 – 900 cm^{-1}) and B–C (900 – 1100 cm^{-1}).

The composition of the newly synthesized materials (Table 2) show, that the Si:B ratio of 1:1, as prefixed in each precursor molecule, is exactly transferred into the final ceramic. In line with the conceptual design of the single source precursors, the chemical compositions of the silicon boron carbonitrides confirm, that carbon has been incorporated into the random inorganic networks to a high degree, most likely

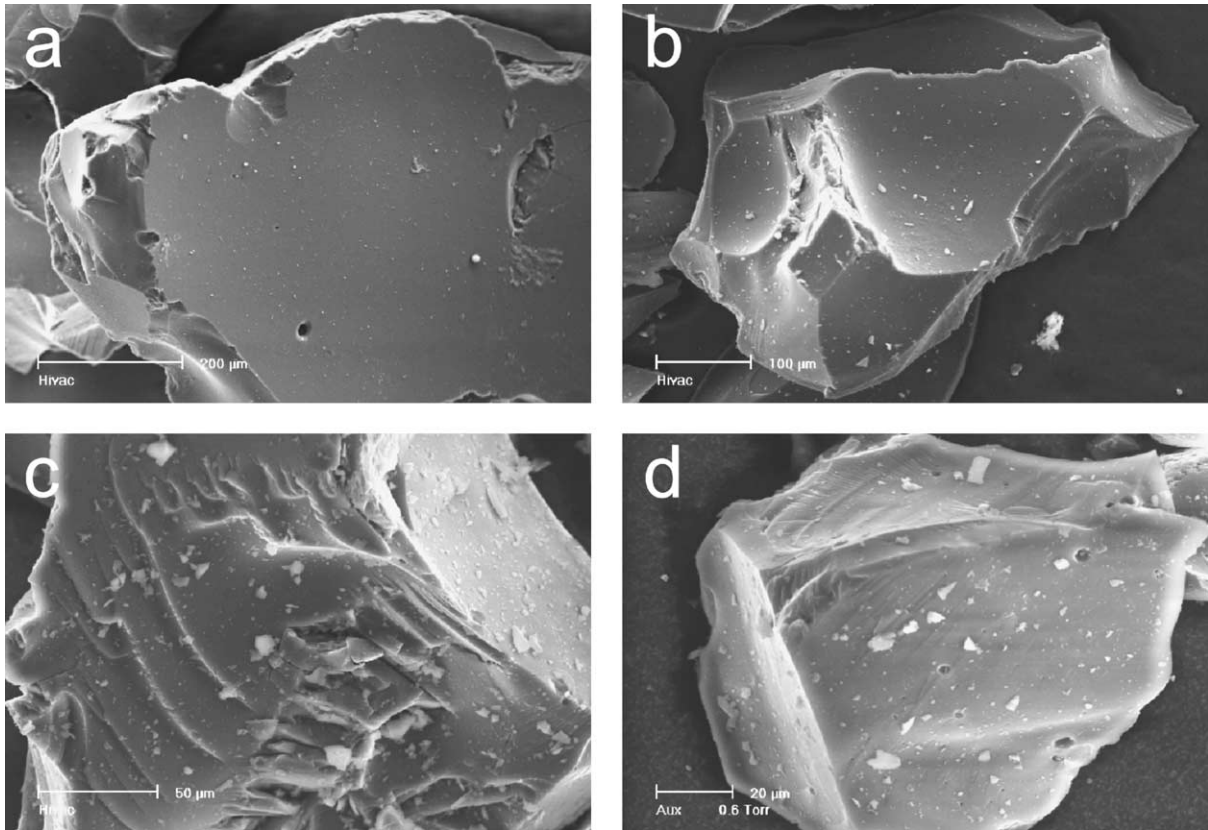


Fig. 2. Scanning electron micrographs of the ceramics derived from TSDM (a), DSDM (b), TSMB (c) and DSMB (d).

caused by the bridging methylene function. Due to the additional silicon bonded methyl group present in the precursors DSDM and DSMB, the appropriate ceramics exhibit a significant higher amount of carbon as in the case for those derived from TSDM and TSMB.

The macroscopic densities of the as-obtained ceramics (Table 3) are rather similar, and seem not to be related to the chemical composition of the carbonitrides or to the structure of the respective single source precursors. However, the values are approximately 30% below the densities of compa-

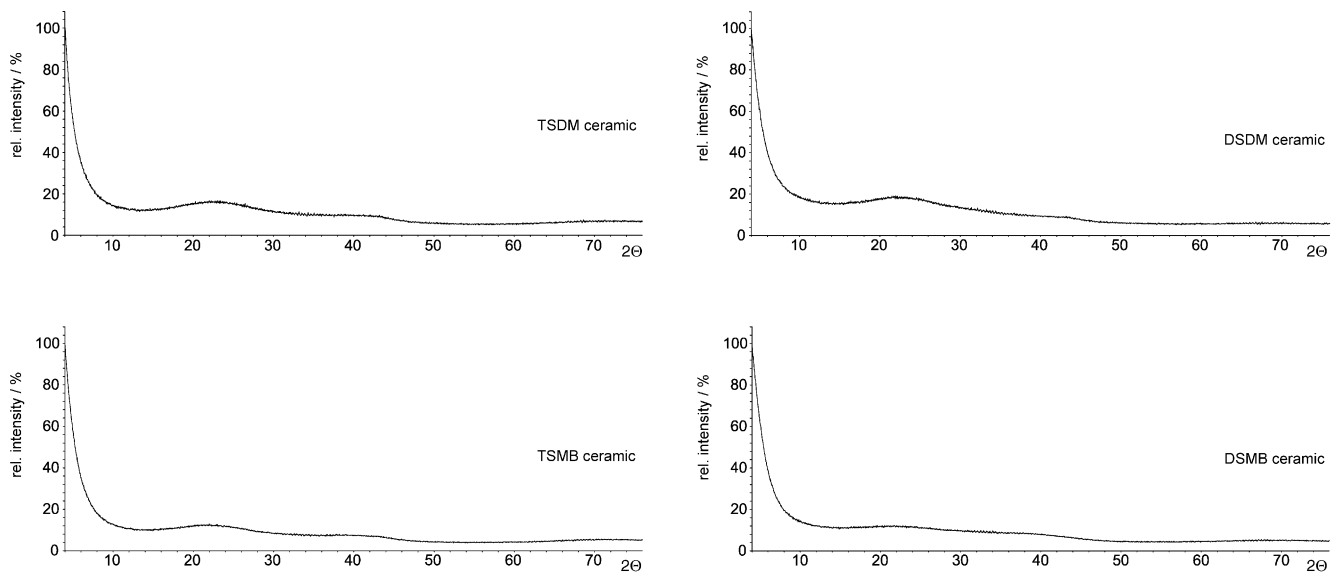


Fig. 3. XRD powder patterns of the prepared Si/B/N/C ceramics after annealing at 1500 °C.

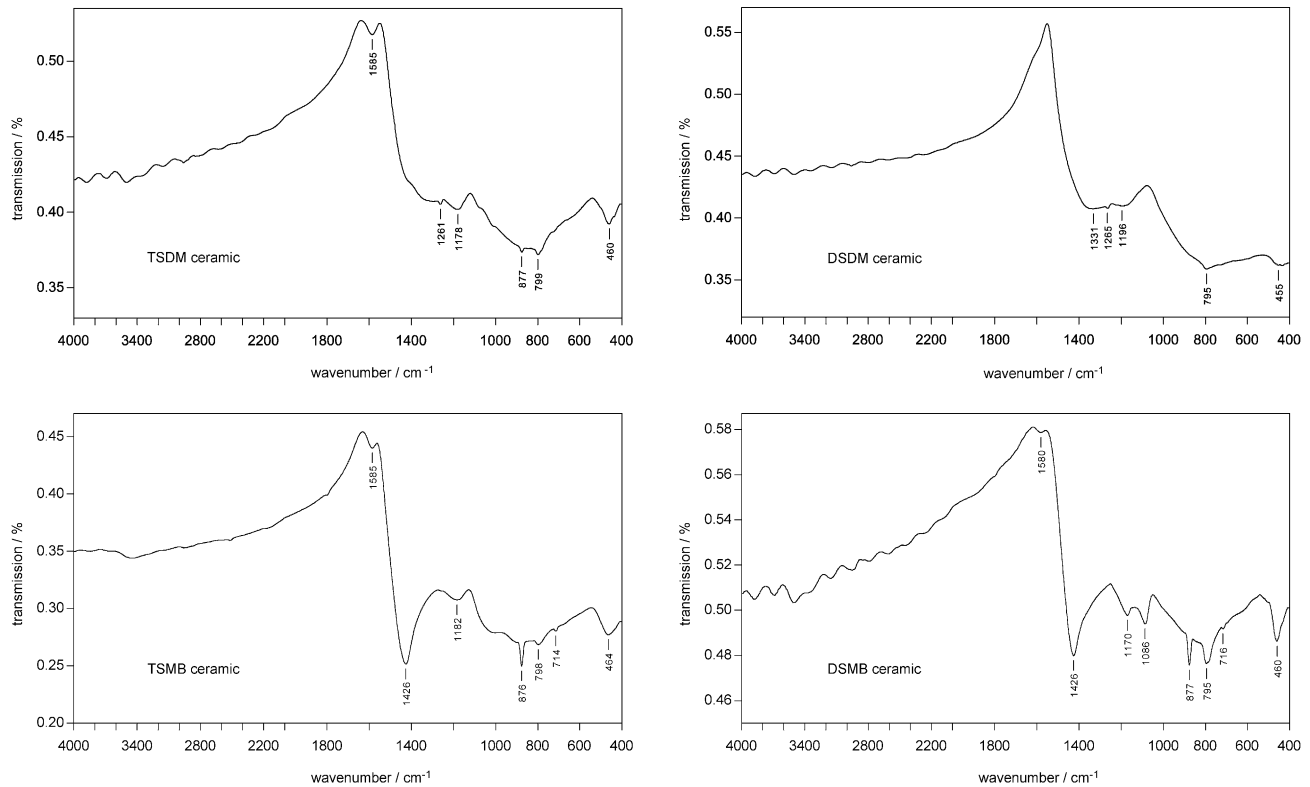


Fig. 4. Infrared spectra of the prepared Si/B/N/C ceramics (KBr pellets).

Table 2

Chemical composition of the synthesized Si/B/N/C ceramics (indicated as mass%)

Ceramic derived from	Si	B	N	C	O	Empirical formulae	
						Exact	Approximately
TSDM	30.7	11.6	34.8	20.8	1.4	Si _{1.0} B _{1.0} N _{2.3} C _{1.6} O _{0.1}	Si ₃ B ₃ N ₇ C ₅
DSDM	30.5	12.3	26.8	30.8	0.8	Si _{1.0} B _{1.0} N _{1.7} C _{2.3} O _{0.1}	Si ₃ B ₃ N ₅ C ₇
TSMB	31.0	11.7	35.4	16.9	2.2	Si _{1.0} B _{1.0} N _{2.3} C _{1.3} O _{0.1}	Si ₃ B ₃ N ₇ C ₄
DSMB	33.7	13.0	27.2	23.3	1.1	Si _{1.0} B _{1.0} N _{1.6} C _{1.6} O _{0.1}	Si ₃ B ₃ N ₅ C ₅

Table 3

Macroscopic densities of the synthesized amorphous Si/B/N/C ceramics in comparison with densities of other known amorphous and crystalline non-oxide ceramics (standard deviation in parentheses)

Precursor/crosslinking reagent	Empirical formula	Macroscopic density (g cm ⁻³)	Structure
TSDM/methylamine	Si ₃ B ₃ N ₇ C ₅	1.9272(4)	Amorphous
DSDM/methylamine	Si ₃ B ₃ N ₅ C ₇	1.9306(2)	Amorphous
TSMB/methylamine	Si ₃ B ₃ N ₇ C ₄	1.9242(7)	Amorphous
DSMB/methylamine	Si ₃ B ₃ N ₅ C ₅	1.9467(8)	Amorphous
TADB/methylamine	Si ₃ B ₃ N ₇ C _{2.4}	1.8372(4)	Amorphous
TADB/ammonia	Si ₃ B ₃ N ₇	1.988(2)	Amorphous
	α-SiC, β-SiC	3.21 [21,22]	Crystalline
	α-Si ₃ N ₄	3.18 [23]	Crystalline
	β-Si ₃ N ₄	3.20 [23]	Crystalline
	h-BN	2.34 [24]	Crystalline
	c-BN	3.45 [25]	Crystalline

rable crystalline phases like SiC or Si₃N₄ (Table 3), although no macroscopic porosity in the silicon boron carbonitrides is observed. Investigations on related Si/B/N/C materials revealed that even on a nanometerscale no voids are present.¹⁰ Thus, the observed low densities of the amorphous ceramics seem to be an intrinsic property, indicating a relatively wide meshed random network, possibly containing voids on a sub-nanometer scale.

The high temperature behavior of the ceramics was checked by means of a DTA/TG thermal analysis, heating the samples up to 2000 °C at a rate of 10 K min⁻¹ in a helium flow. Since the ‘onset’ of weight loss upon heating up Si/B/N/C ceramics often starts at about 1850 °C, being generally rather shallow, this single value is not suitable for a valid comparison of different ceramic materials in terms of high temperature stability. Instead, a more reasonable item for the evaluation of high temperature stabilities is the final percentage weight loss at the maximum temperature of the measurement. Thus, on heating up to 2000 °C, the TSDM ceramic loses 19% of its weight, the DSDM ceramic 12%, the TSMB ceramic 11%, and for the DSMB ceramic no mass loss was detectable at all. From the DTA/TG measurements it can be seen that the thermal durability of the investigated samples correlates with both, the carbon content and with the presence of borazine rings present in the amorphous network (Fig. 5). Thus, on the one hand, the carbon richer ceramics derived from DSDM and DSMB exhibit a lower mass loss than those derived from TSDM and TSMB. On the other hand, the TSMB and the DSMB ceramic (both with incorporated borazine rings) lose less weight than the ceramics derived from the acyclic precursors TSDM and DSDM. Combining both, a high carbon content as well as incorporated borazine rings, the DSMB ceramic exhibits the best thermal durability of the four investigated silicon boron carbonitrides. The thermal stability of the new carbonitrides was also tested in a flow

of pure oxygen. On heating the samples up to 1300 °C at a rate of 10 K min⁻¹, no oxidation or degradation process happened. Instead, a slight increase in weight (2.1–2.8%) could be detected at the maximum temperature, indicating the formation of a thin passivating surface layer,³ thus preventing the ceramic from being further oxidized.

In order to gain some information about micromechanical properties of the new materials, the microhardness (H) and elastic modulus (E) of the prepared Si/B/N/C ceramics were investigated using a nanoindenter device. It should be noticed, that the values for H and E measured with such a device generally cannot be compared to the hardness and elastic modulus obtained from other indentation techniques. Since here the imprints are analyzed while load is still applied to the sample (CSM, continuous stiffness measurement), the resulting values for H and E are systematically lower than those obtained via conventional indentation techniques, where the imprints are analyzed after the experiment without load. This effect can be explained regarding the relaxation behavior of the sample. Due to elastic deformation of the sample during the indentation experiment the generated imprint is always somewhat larger while load is applied than it is after load is released. Thus, after a conventional indentation experiment the generated imprint is always too small suggesting systematically too high values for the hardness and for the stiffness.

The measured values for H and E are summarized in Table 4 together with data reported for other amorphous and crystalline non-oxide materials, all characterized by means of nanoindentation. It turns out, that the hardness and the stiffness of the carbon enriched ceramics derived from DSDM and DSMB are higher than it is the case for the samples derived from TSDM and TSMB, reflecting the more pronounced covalent character of the Si–C bond compared to the Si–N bond. Furthermore, the ceramics with incorporated borazine rings (derived from TSMB and DSMB) are harder and

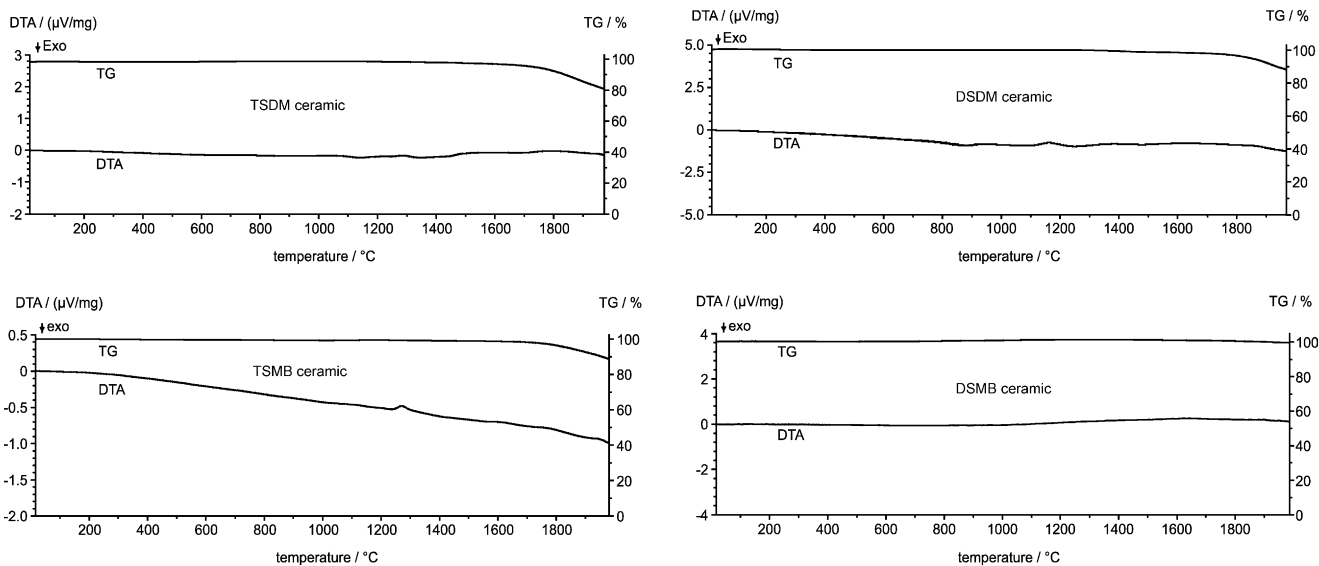


Fig. 5. DTA/TG curves of prepared Si/B/N/C ceramics upon heating up to 2000 °C in a helium flow at 10 K min⁻¹.

Table 4
Microhardness and elastic modulus of the prepared Si/B/N/C ceramics in comparison with other materials characterized by nanoindenter experiments

Sample	Microhardness (GPa)	Elastic modulus (GPa)
TSDM ceramic ($\text{Si}_3\text{B}_3\text{N}_7\text{C}_5$)	8.5 ± 0.2	91 ± 2
DSDM ceramic ($\text{Si}_3\text{B}_3\text{N}_5\text{C}_7$)	14.4 ± 0.2	123 ± 8
TSMB ceramic ($\text{Si}_3\text{B}_3\text{N}_7\text{C}_4$)	11.4 ± 0.8	107 ± 8
DSMB ceramic ($\text{Si}_3\text{B}_3\text{N}_5\text{C}_5$)	14.5 ± 0.6	127 ± 8
Quartz glass	8.9 ± 0.04 [19]	72.0 [20]
$\text{SiC}_{0.67}\text{N}_{0.80}$ (amorphous) [19]	13 ± 2	121 ± 10
Si_3N_4 (crystalline) [19]	24.9 ± 0.6	220 ± 10
SiC (crystalline) [19]	35 ± 2	300 ± 10

stiffer than their counterparts derived from the acyclic precursors TSDM and DSDM, clearly indicating that in these materials have been reinforced through the incorporation of rigid structural units. Compared to quartz glass, the new Si/B/N/C materials exhibit higher values for H and E, being in good accordance with the values reported for an amorphous Si/C/N compound.¹⁹ Comparing the hardness and elastic modulus of the amorphous materials with crystalline samples (Table 4), it turns out that crystalline samples are generally tougher than comparable amorphous compounds. An explanation for this might be found in the structural disorder of the random networks, which leads to a compressible local free-volume, and thus to a certain softening of the material.

4. Conclusions

With the synthesis of the new amorphous silicon boron nitrides $\text{Si}_3\text{B}_3\text{N}_7\text{C}_5$, $\text{Si}_3\text{B}_3\text{N}_5\text{C}_7$, $\text{Si}_3\text{B}_3\text{N}_7\text{C}_4$ and $\text{Si}_3\text{B}_3\text{N}_5\text{C}_5$, it has been shown that the high temperature durability of such compounds can be raised significantly by both, increasing the carbon content, and by the incorporation of borazine rings as rigid structural elements. This has been achieved by an adequate design of the single source precursors from which the ceramics were derived. Thus, carbon was incorporated into the Si/B/N/C ceramics at a high degree through a methylene bridge interconnecting silicon and boron. Additionally, by choosing a borazine derivative as precursor molecule, borazine rings were introduced into the final ceramics, causing a further improved thermal stability and hardness of the silicon boron carbonitrides compared to those derived from precursors without cyclic units.

The increased high temperature stability of carbon-rich compositions can be ascribed to the fact that carbon bonds to four neighbors via strong covalent bonds instead of three in the case of nitrogen. The additional incorporation of borazine rings into a Si/B/N/C random network further increases the high temperature durability since these rigid units make the covalent Si/B/N/C network stiffer and stronger due to strong $p_\pi-p_\pi$ interactions between boron and nitrogen. As a consequence, conformational changes as well as reorientation of atoms, which always precede decomposition, are significantly suppressed. The supposed microscopic increase in rigidity, also reflects in enhanced macroscopic properties

like raised hardness and stiffness, as observed in the ceramics derived from the borazine precursors.

The material properties of the silicon boron carbonitride derived from DSMB clearly show, that combination of a high carbon together with incorporated rigid structure elements like borazine rings leads to a maximum temperature durability (≥ 2000 °C) as well as to high values for the microhardness and elastic modulus.

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