

New Si/B/N/C Ceramics from a Silaborazine-Type Single-Source Precursor

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received November 25, 2010; accepted December 2, 2010

Abstract

A new chloro-substituted monocyclic silaborazine derivative with a B/Si-ratio of 2, namely 1,1,3,5-tetrachloro-2,6-dimethyl-4-hydride-1-silaborazine (TDSB), has served as a single-source precursor for the synthesis of amorphous Si/B/N/C ceramics via the well-known “polymer route”. Accordingly, ammonia and methylamine were used as cross-linking reagents for polymerization of TDSB, leading to highly homogeneous pre-ceramic polymers, which were characterized with spectroscopic methods. In addition, subsequent thermal degradation of as-obtained polyborocarbosilazanes was monitored by means of DTA/TG/MS up to 1350 °C. The resulting amorphous ceramics exhibit excellent thermal durability up to 2000 °C under inert conditions. This is attributed to silaborazine rings (originating from the TDSB precursor molecule) still being present in the covalent Si/B/N/C network and reinforcing the final ceramics on atomic scale by acting as rigid structural units.

Keywords: Silaborazine, single-source precursor, pre-ceramic polymer, precursor-derived ceramic, Si/B/N/C ceramics

I. Introduction

Amorphous Si/B/N/C ceramics fulfil basic requirements for a variety of application areas, particularly under extreme conditions, such as in the aviation and aerospace industries. This is mainly due to their low density, low thermal coefficient of expansion, low thermal conductivity, high thermal shock resistivity, high chemical resistivity and good mechanical properties, especially at high temperatures^{1–5}. Thus far, the only feasible approach for the production of Si/B/N/C ceramics seems to be the “polymer route”⁵, which includes polymerization of a molecular, so-called single-source precursor. This precursor needs to already contain the constituent elements in the correct linkage of the final ceramic. Subsequent pyrolysis of the resulting pre-ceramic polymer yields the all-inorganic final ceramic¹.

The choice of single-source precursor is one of the key factors for influencing the properties and performance of the final Si/B/N/C ceramics. For example, their thermal durability increases with higher carbon content⁶. Even better, incorporation of rigid structural elements into the random networks, e.g. borazine rings, has been shown to significantly improve the hardness, stiffness and thermal durability of Si/B/N/C ceramics⁷. This was attributed to the presence of highly inflexible borazine rings, which strengthen the covalent Si/B/N/C network as a rigid backbone, making the whole network stiffer and stronger. Almost all of the borazine-type single-source precursors contain a carbon linkage between boron and silicon atoms, which most probably forms more dangling

bonds in the random network^{7–9}. The only borazine-type single-source precursors $[(\text{SiCl}_3)\text{NB}(\text{Cl}_n(\text{CH}_3)_{1-n})]_3$ in which silicon is directly attached to the borazine ring via nitrogen atoms have very recently been reported¹⁰. Maintaining the advantage of having a ring in the structure, silaborazine-type single-source precursors in which silicon forms a constitutional part of the borazine ring are promising candidates for Si/B/N/C ceramics. Up to now, only polycyclic silaborazine derivatives were used as single-source precursors for Si/B/N/C ceramics, and showed improved high-temperature stability compared to their acyclic counterparts^{11, 12}.

In this paper, we report on the preparation of new amorphous Si/B/N/C ceramics from the first chloro-substituted monocyclic silaborazine derivative, namely 1,1,3,5-tetrachloro-2,6-dimethyl-4-hydride-1-silaborazine (TDSB)¹³ via a thermal polymer-to-ceramic conversion. TDSB contains chlorine atoms bonded directly to silicon and boron atoms, which allows a very rapid and quantitative cross-linking with nitrogen bases, such as methylamine or ammonia, via dehydrohalogenation reactions. The other unique feature of TDSB is its B/Si-ratio of 2, which differs distinctly from the so far explored ones of 1, opening access to new Si/B/N/C ceramics.

II. Experimental

(1) General procedures

All reactions were performed in a purified argon atmosphere using either standard Schlenk techniques or inside a glove box. Freshly distilled hexane (> 99 %, Merck) was used. Commercially available methylamine (99.5 %, Gerling Holz & Co) and ammonia (99.999 % for reaction and

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99.998 % for pyrolysis, Westfalen AG) were used directly without further purification.

(2) Characterization techniques

FT-IR spectra were recorded between 400 and 4000 cm^{-1} on a Bruker IFS 113v FT-IR spectrometer, using KBr pellets. Powder diffraction data for air-insensitive ceramics have been collected with a laboratory diffractometer in the Bragg-Brentano geometry (Bruker D8 with Lynx-Eye position-sensitive detector with a 3.5° opening angle and $\text{CuK}_{\alpha 1}$ radiation from primary Ge(111)-Johansson-type monochromator). A Si(911)-zero-background sample holder was used and the sample was rotated during data collection. For air-sensitive polymers, powder X-ray diffraction patterns were recorded by a STOE Stadi-P diffractometer in Debye-Scherrer geometry, using germanium-monochromated $\text{CuK}_{\alpha 1}$ radiation and a position-sensitive detector in a sealed glass capillary ($\varnothing = 0.5 \text{ mm}$). The quantitative analyses of nitrogen, oxygen and carbon were obtained by using carrier gas heat extraction analyzers TC-436 and C-200 (LECO, St. Joseph, MI, USA). Boron and silicon were determined with an optical emission spectrometer equipped with inductively coupled plasma (either ARL 3580 B (EcuBlens, Switzerland) or Vista Pro Simultaneous (Varian, Darmstadt, Germany)). The thermal behaviour of the pre-ceramic polymers up to 1350 $^\circ\text{C}$ was investigated by means of simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) (Netzsch STA 409, heating rate 10 K min^{-1} , argon or oxygen flow) equipped with a quadrupole mass spectrometer (MS) (Blazer MS421). High-temperature-DTA/TG analysis of the ceramics up to 2000 $^\circ\text{C}$ was performed with a thermal analyzer (Netzsch STA 409C, heating rate 10 K min^{-1} , helium flow).

(3) Preparation of pre-ceramic polymers

The single-source precursor molecule TDSB was synthesized according to a previously described procedure¹³. The prominent structural unit of TDSB is clearly the silaborazine ring, which is supposed to become an integral part of the final covalent Si/B/N/C network after polymerization and pyrolysis. Owing to chlorine atoms bonded to silicon and boron atoms, cross-linking of the TDSB single-source precursor with nitrogen bases, such as methylamine or ammonia, is possible and should proceed very rapidly and quantitatively via dehydrohalogenation reactions. Two different pre-ceramic polymers were prepared from the TDSB molecule via polycondensation with either ammonia or methylamine (referred to in the following as P-TDSB-1 and P-TDSB-2, respectively). For preparation of P-TDSB-1, a solution of 1.71 g (6.5 mmol) TDSB in 20 ml hexane was added dropwise to solution of 16.66 ml (11.33 g, 0.67 mol) liquid ammonia in 80 ml hexane at -78°C under argon flow. The stirred mixture was allowed to reach room temperature, whereupon excessive ammonia evaporated, and NH_4Cl and the polymer in hexane remained in the flask. After removal of hexane under vacuum in a cold trap, the white solid residue was sublimed overnight to remove NH_4Cl at 210 $^\circ\text{C}$ and 1.3×10^{-3} mbar, and pure P-TDSB-1 was obtained. Similarly, for the prepara-

tion of P-TDSB-2, a solution of 2.35 g (8.9 mmol) TDSB in 20 ml hexane was added dropwise to solution of 40 ml (27.76 g, 0.89 mol) liquid methylamine in 80 ml hexane at -78°C under argon flow. The stirred mixture was allowed to reach room temperature, whereupon excessive methylamine evaporated, and methylamine chloride precipitated. After filtrating off methylamine chloride, the residue was washed three times with 10 ml hexane. When hexane was removed from the filtrate under vacuum in a cold trap, the pre-ceramic polymer P-TDSB-2 remained as a viscous colourless liquid, which was further annealed for solidification at 100 $^\circ\text{C}$ for 5 h.

(4) Preparation of Si/B/N/C ceramics

The amorphous Si/B/N/C ceramics were prepared via pyrolytic conversion of the pre-ceramic polymers, followed by subsequent calcination. In a typical experiment, the pre-ceramic polymer is loaded into an inerted boron nitride crucible, which is placed in a quartz tube. Under a slight flow of argon (or ammonia), the sample is heated in a horizontal furnace up to 300 $^\circ\text{C}$ with a 100 $^\circ\text{C h}^{-1}$ heating rate followed by a dwelling period of three hours to complete cross-linking of the polymer. Subsequently, the temperature is raised to 900 $^\circ\text{C}$ with 100 $^\circ\text{C h}^{-1}$ and kept for 3 h, and then reduced to room temperature. In a final step, the pyrolysed sample is calcined at 1400 $^\circ\text{C}$ (heated with 10 $^\circ\text{C min}^{-1}$ rate) for 3 h under argon (or N_2) flow in a corundum tube. Three different Si/B/N/C ceramics were prepared. Two of them were prepared from the pre-ceramic polymers P-TDSB-1 and P-TDSB-2 with pyrolysis up to 900 $^\circ\text{C}$ followed by calcination at 1400 $^\circ\text{C}$ only under argon flow, and referred as C-TDSB-1 and C-TDSB-2, respectively. The third ceramic was obtained from P-TDSB-1 polymer with pyrolysis up to 900 $^\circ\text{C}$ under NH_3 flow and calcination at 1400 $^\circ\text{C}$ under N_2 flow (referred as C-TDSB-3).

III. Results and Discussion

(1) Characterization of the pre-ceramic polymers

Pre-ceramic polymers have been synthesized via dehydrohalogenation reactions of the new silaborazine-type single source precursor, TDSB, with ammonia (P-TDSB-1) and methylamine (P-TDSB-2). As expected, the as-synthesized P-TDSB-1 polymer is an insoluble solid in hexane owing to the higher degree of cross-linking achieved using ammonia. In contrast, the as-synthesized P-TDSB-2 polymer is a viscous liquid and soluble in organic solvents, e.g. hexane. The powder X-ray diffractograms of both polymers reveal that they are amorphous (Fig. 1a for P-TDSB-1 and Fig. 1b for P-TDSB-2). The FT-IR spectra of P-TDSB-1 and P-TDSB-2 are shown in Fig. 2b and Fig. 2c, respectively. As one would expect, the absorptions of both polymers resemble those observed in the FT-IR spectrum of the pristine TDSB (Fig. 2a), particularly with regard to the strong bands at 3380–3470 cm^{-1} , 2800–2980 cm^{-1} and 1350–1480 cm^{-1} , which are correlated to NH groups, methyl groups and silaborazine rings, respectively. A significant increase in intensity of the band at 3417 cm^{-1} (resulting from NH groups) for P-TDSB-1

polymer compared to the TDSB and P-TDSB-2 polymer clearly confirms the presence of new terminal Si-NH₂ and B-NH₂, and bridging SiN(H)Si, SiN(H)B and BN(H)B groups, which were introduced during polycondensation with ammonia. Similarly, the absorption bands between 2800 and 2980 cm⁻¹ (resulting from CH₃ groups) in P-TDSB-2 polymer appear much stronger compared to the TDSB and P-TDSB-1 polymer, indicating the presence of new terminal Si-NH(CH₃) and B-NH(CH₃), and bridging SiN(CH₃)Si, SiN(CH₃)B and BN(CH₃)B groups, which were introduced during polycondensation with methylamine.

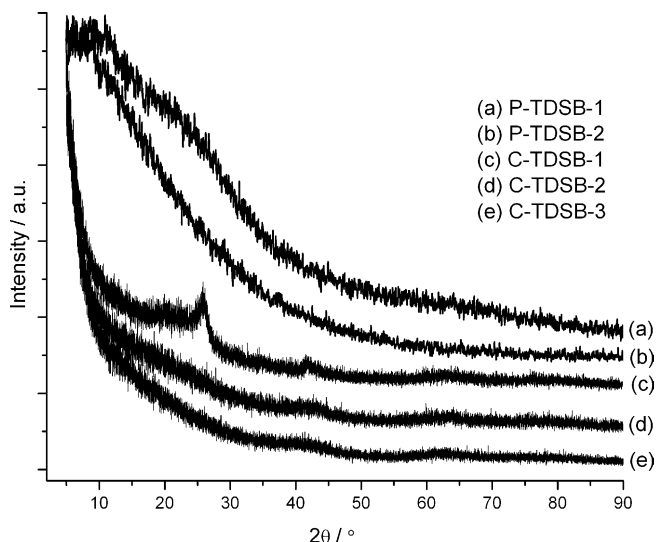


Fig. 1: Powder X-ray diffractograms of a) P-TDSB-1 polymer, b) P-TDSB-2 polymer, c) C-TDSB-1 ceramic, d) C-TDSB-2 ceramic and e) C-TDSB-3 ceramic.

(2) Pyrolytic conversion of the pre-ceramic polymers

The pyrolytic conversions of the P-TDSB-1 and P-TDSB-2 polymers into amorphous Si/B/N/C ceramics were monitored with the simultaneous DTA/TG/MS technique. In analogy to the thermal degradation of previously reported pre-ceramic polyborocarbosilazanes⁵, the pyrolyses of P-TDSB-1 and P-TDSB-2 pre-ceramic polymers proceed in mainly two well-resolved stages, as presented in Fig. 3 and Fig. 4, respectively. In the first step between 200 and 600 °C, the P-TDSB-1 polymer loses 29.7 % of its initial mass under evolution of mainly ammonia, indicating further polycondensation and cross-linking of the corresponding polymer. The second step between 600 and 1090 °C is mainly characterized by the evolution of methane, probably originating from the methyl groups on the silaborazine ring of the polymer. During this stage, a mass loss of 22.2 % was observed for P-TDSB-1. Above 1090 °C, a slight decrease in mass of 7.6 % for P-TDSB-1 was observed, resulting from the evolution of nitrogen and hydrogen. Consequently, an overall ceramic yield of 40.5 % for P-TDSB-1 was obtained for the thermal conversion of the TDSB-derived pre-ceramic polymer into the corresponding Si/B/N/C ceramics. Similar to the P-TDSB-1 polymer, P-TDSB-2 polymer loses 35.8 % of its initial weight between 200 and 380 °C, mainly as a result of the evolution of methylamine. Between 380 and 645 °C, the P-TDSB-2 polymer loses an additional 13.9 % weight mainly due to releasing methyl groups both from the silaborazine rings and from the bridging nitrogen atoms. Further heating up to 1350 °C results in only 4.8 % weight loss. Finally, 54.5 % ceramic yield has been attained for P-TDSB-2 polymer at 1350 °C.

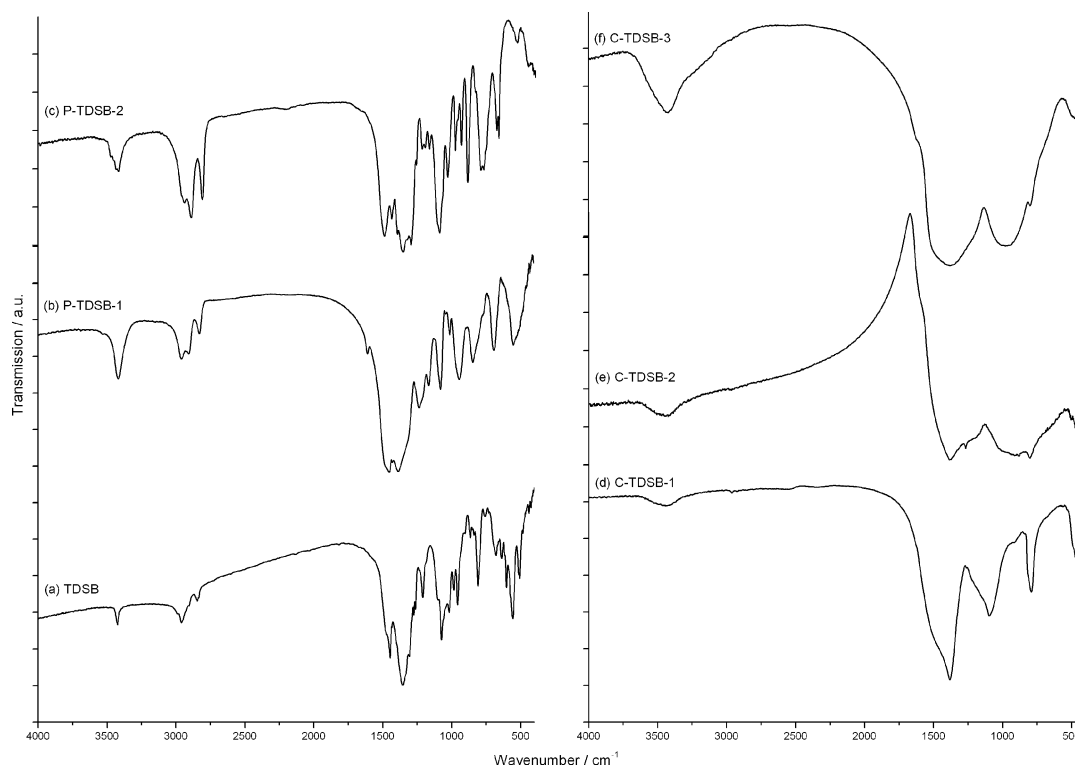


Fig. 2: FT-IR spectrum of a) TDSB, b) P-TDSB-1 polymer, c) P-TDSB-2 polymer, d) C-TDSB-1 ceramic, e) C-TDSB-2 ceramic and f) C-TDSB-3 ceramic.

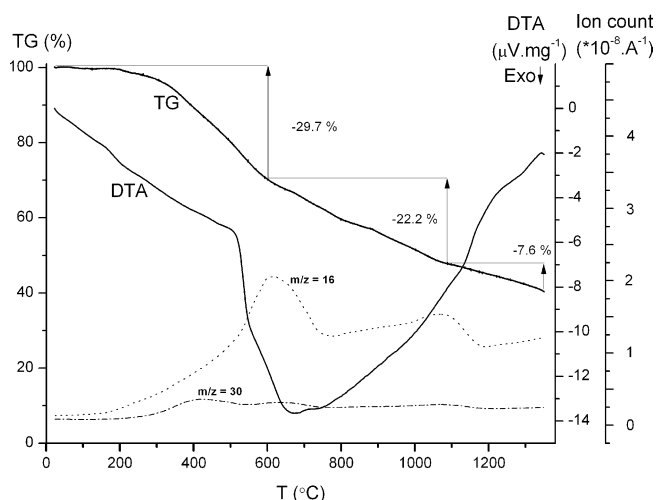


Fig. 3: DTA/TG/MS thermogram of P-TDSB-1 polymer.

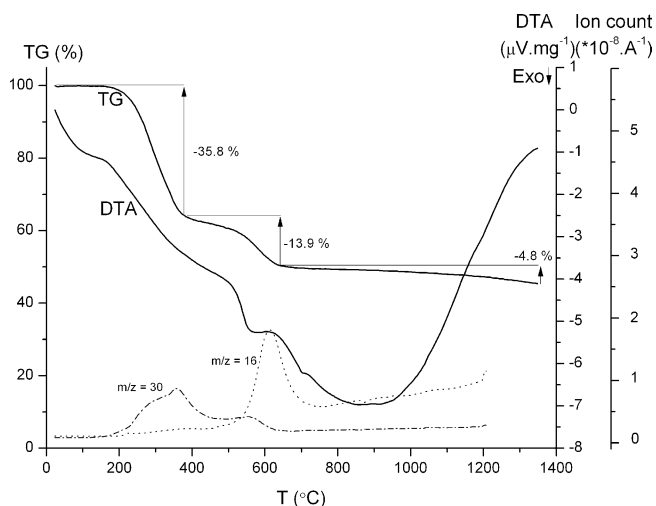


Fig. 4: DTA/TG/MS thermogram of P-TDSB-2 polymer.

(3) Characterization of Si/B/N/C ceramics

The amorphous Si/B/N/C ceramics have been prepared via pyrolytic conversion of the pre-ceramic polymers, P-TDSB-1 and P-TDSB-2. The amorphous character of the as-synthesized ceramics was confirmed by means of powder X-ray diffraction analysis (Fig. 1c for C-TDSB-1, Fig. 1d for C-TDSB-2 and Fig. 1e for C-TDSB-3). On the other hand, for C-TDSB-1, broad reflections at $2\theta = 26^\circ$ and 42° can be assigned to the formation of slightly turbostratic h-BN phases. BN occurring already at lower temperatures is possibly due to the higher B content (B/Si-ratio of 2 in TDSB). Polymerization of TDSB with NH_3 yields a high degree of cross-linking and thus a stiffer network. When P-TDSB-1 polymer is pyrolysed under argon atmosphere, partial decomposition of silaborazine rings – particularly via silazane cleavage – forms more stable BN units. However, when the same polymer is pyrolysed under NH_3 atmosphere up to 900°C , the formation of BN units is significantly suppressed. For that reason, no such BN formation was observed in C-TDSB-3 after 1400°C . Similar turbostratic h-BN phases were rarely observed in previously described Si/B/N/C ceramics. Very recently, such phases were reported when amorphous $\text{SiBN}_{2.5}\text{C}_{1.2}\text{O}_{0.1}$ was spark-plasma-sintered,

which caused partial decomposition of the amorphous phase into crystalline fine-grained SiC and turbostratic h-BN phases¹⁴. These phases were distinguished by means of energy-filtered TEM analysis. In another paper, thermal decomposition of SiN_4 units connecting the borazine rings in SiBN_3C ceramics, obtained from $[(\text{SiCl}_3)\text{NB}(\text{Cl}_n(\text{CH}_3)_{1-n})_3]$, has been reported to result in BN phases at $T > 1800^\circ\text{C}$ ¹⁰.

The elemental analyses of the new as-synthesized Si/B/N/C ceramics resulted in the Si:B ratio of 1:2, which is exactly the same as in the precursor TDSB molecule, with oxygen impurities less than 1 wt %. FT-IR spectra of C-TDSB-1, C-TDSB-2 and C-TDSB-3 ceramics are presented in Fig. 2d, Fig. 2e and Fig. 2f, respectively. The broad but very strong IR absorption of all three ceramics between 1350 and 1450 cm^{-1} can undoubtedly be assigned to the anti-symmetric stretching mode of the silaborazine ring, which was observed not only in other silaborazines¹⁵ but also in both TDSB molecule and the polymers made from TDSB. Thus, silaborazine rings introduced via the single-source precursor TDSB have become a part of the final random networks. Other typical structural increments can also be identified from their corresponding broad bands, i.e. for Si-N between 1070 – 1130 cm^{-1} and 440 – 480 cm^{-1} , and for B-N between 770 and 810 cm^{-1} .

The high-temperature behaviour of the ceramics from TDSB has been investigated with DTA/TG analysis. Even though the decomposition of the amorphous network in all ceramics starts at around 1400°C , only 2.5 % weight loss for C-TDSB-1 (Fig. 5), 1.2 % for C-TDSB-2 (Fig. 6) and 0.9 % for C-TDSB-3 (Fig. 7) were observed at 1910°C . These very low weight losses are attributed to the silaborazine rings, which should be tightly integrated into the random network serving as a rigid structural element. Powder X-ray diffractograms of C-TDSB-1, C-TDSB-2 and C-TDSB-3 ceramics after heating up to 2000°C are presented in Fig. 8a, Fig. 8b and Fig. 8c, respectively. The formation of Si_3N_4 and SiC domains (as in all new Si/B/N/C ceramics) is a typical high-temperature decomposition process of Si/B/N/C ceramics, whereas the observation of crystalline silicon (in C-TDSB-3 ceramic) and BN (in C-TDSB-1 ceramic) is quite rare. Thus far, the formation of elemental silicon was observed only in few Si/B/N/C ceramics, i.e. $\text{SiB}_{0.5}\text{N}_{1.5}\text{C}$ ¹⁶ (from an acyclic precursor), $\text{SiB}_{1.4}\text{N}_{2.2}\text{C}_{0.9}\text{O}_{0.2}$ ^{11, 12} (from a polycyclic silaborazine-type precursor) and $\text{SiBN}_3\text{C}_{0.9}\text{O}_{0.1}$ ^{11, 12} (from a borazine-type precursor), and attributed to thermal decomposition of intermediate Si_3N_4 under evolution of nitrogen. On the other hand, in C-TDSB-1, the formation of turbostratic h-BN phases was already observed to occur above 1400°C , and they thus still exist after heating to 2000°C . Formation of SiC in C-TDSB-1 above 2000°C indicates that partial decomposition of the silaborazine ring during pyrolysis actually occurs and silicon-containing units form stable SiC phases with carbon atoms in the network. However, in C-TDSB-3, similar silicon-containing units mainly form elemental silicon phases (owing to a lack of carbon atoms) and few Si_3N_4 phases.

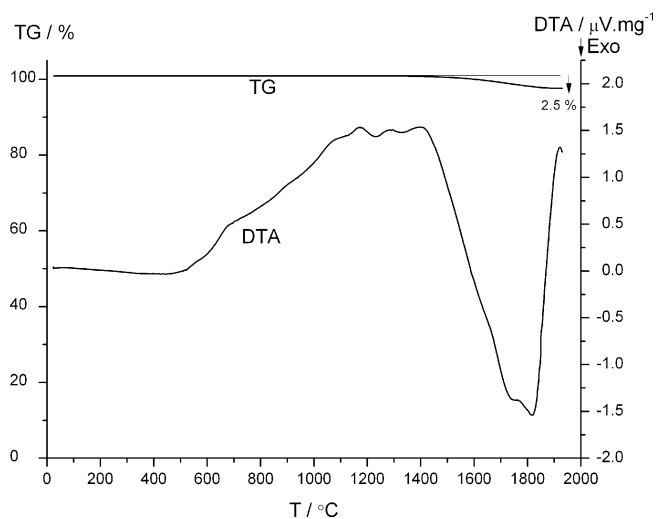


Fig. 5: High-temperature-DTA/TG thermogram (heating cycles) of C-TDSB-1.

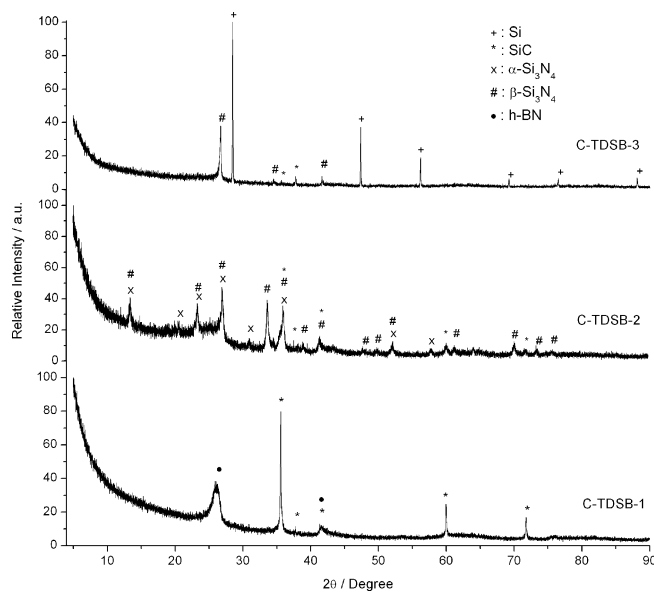


Fig. 8: Powder X-ray diffractograms of a) C-TDSB-1, b) C-TDSB-2 and c) C-TDSB-3 ceramics after 2000 °C.

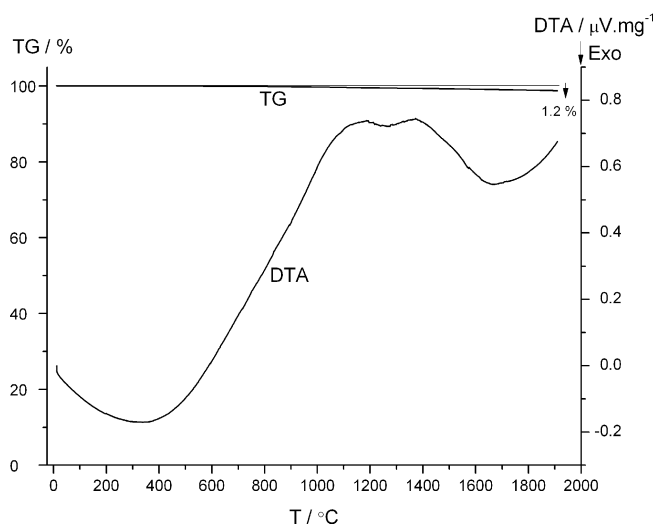


Fig. 6: High-temperature-DTA/TG thermogram (heating cycles) of C-TDSB-2.

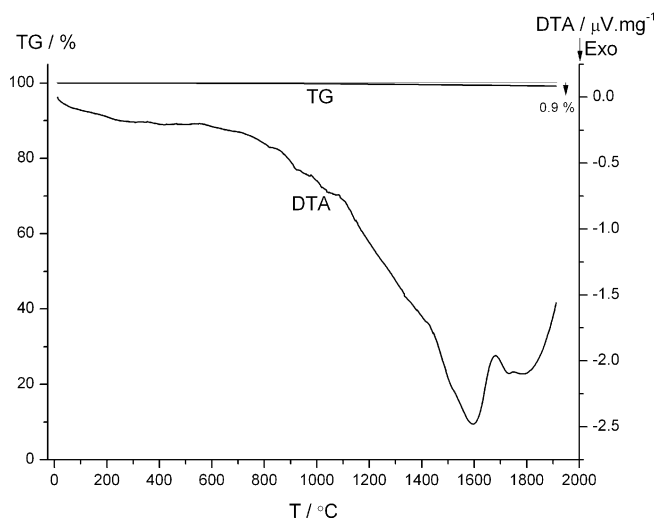


Fig. 7: High-temperature-DTA/TG thermogram (heating cycles) of C-TDSB-3.

Stability of ceramics at high temperatures under atmospheric conditions is crucial for various applications. Therefore, thermal analysis of the ceramics derived from TDSB was performed up to 1300 °C in a flow of pure oxygen with 10 K min⁻¹ heating rate (Figs. 9, 10 and 11 for C-TDSB-1, C-TDSB-2 and C-TDSB-3, respectively). Among the new ceramics, C-TDSB-2 shows the strongest resistance to oxidation and only 2.5 % in weight increase occurs, possibly due to the formation of a passivating surface double-layer preventing further oxidation². On the other hand, C-TDSB-1 and C-TDSB-3 have moderate oxidation stability. C-TDSB-2 shows an insignificant mass loss up to 940 °C, but then a 17.52-% increase in weight up to 1300 °C was observed. In the case of C-TDSB-3, a 6.6-% weight loss was observed at 370 °C and stayed unchanged up to 700 °C, after which a constant weight increase (12.4 %) was observed up to 1300 °C. These results show that stiffer ceramics (i.e. C-TDSB-1 and C-TDSB-3 due to cross-linking via NH₃) are less resistive to heating owing to a lower degree of flexibility when exposed to thermal energy, which also results in further oxidation on the surfaces.

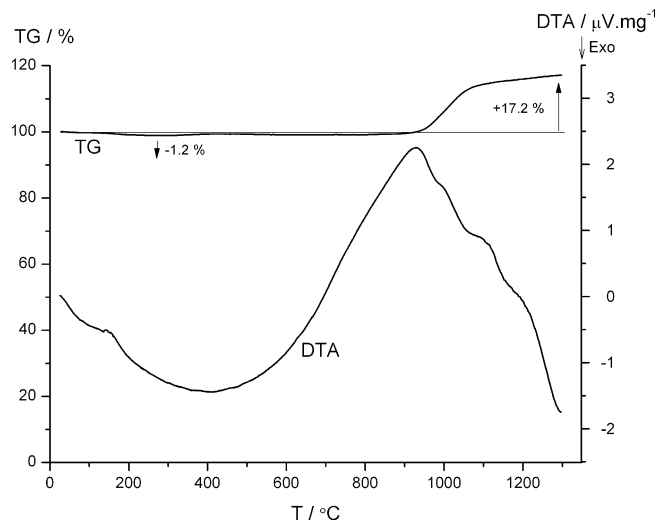


Fig. 9: DTA/TG curves of as-prepared C-TDSB-1 ceramic upon heating up to 1300 °C in a flow of pure oxygen at 10 K min⁻¹.

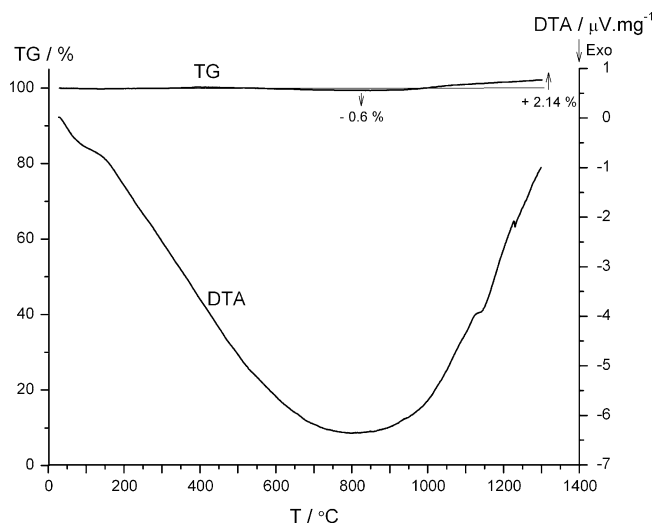


Fig. 10: DTA/TG curves of as-prepared C-TDSB-2 ceramic upon heating up to 1300 °C in a flow of pure oxygen at 10 K min⁻¹.

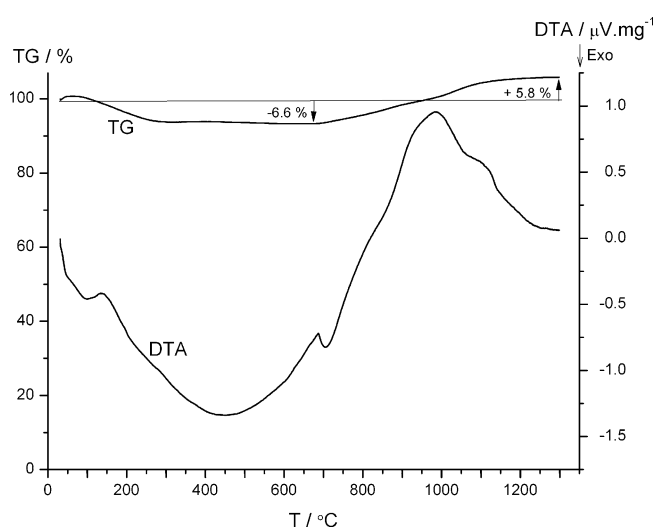


Fig. 11: DTA/TG curves of as-prepared C-TDSB-3 ceramic upon heating up to 1300 °C in a flow of pure oxygen at 10 K min⁻¹.

IV. Conclusions

A new chloro-substituted monocyclic silaborazine derivative, namely 1,1,3,5-tetrachloro-2,6-dimethyl-4-hydride-1-silaborazine (TDSB), has been polymerized with ammonia and methylamine to yield pre-ceramic polymers, which provided amorphous Si/B/N/C ceramics after pyrolysis at a temperature of 1400 °C. The TDSB molecule comprises an important structural feature so that silicon and boron atoms on the monocyclic silaborazine ring are fully chlorinated, which allows direct cross-linking of the silaborazine rings through their constituent elements (Si and B) and a cross-linking agent (e.g. ammonia or amines). This makes the network stiffer and stronger against conformational changes of the structure, which results in very low weight loss at high temperatures. The elemental analyses of new Si/B/N/C ceramics indicate that the same Si:B ratio as in TDSB molecule is achieved. In addition, a very strong IR absorption in all ceramics between 1360 and 1380 cm⁻¹ reveals that the silaborazine rings form part of the final random network. However, the new ceramic materials start to decompose at around

1400 °C with only very small weight losses at 1910 °C. It was also established that the cross-linking agent and thermal history of the final ceramics have a significant effect on their stabilities. When TDSB is cross-linked with NH₃, a highly cross-linked ceramic network is formed, which causes significant amount of BN-rich domains in the final ceramic network. This results in lower thermal stabilities under pure oxygen atmosphere and unusual formation of BN phases at lower temperatures. On the other hand, cross-linking of TDSB with NH₂(CH₃) not only allows enough flexibility in its network upon heating but also significantly incorporates carbon into the final ceramic matrix, resulting in a better resistance to decomposition and oxidation even at higher temperatures. Finally, the new TDSB ceramics appear less stable than the Si/B/N/C ceramics obtained from the previous single-source precursors with B:Si as 1:1 entering the network in an alternating sequence.

Acknowledgement

The authors are grateful to M.-L. Schreiber for supporting preparative and analytical work, and to J. Wilfert and T. Pilz for DTA/TG/MS measurements.

References

- Baldus, H.-P., Wagner, O., Jansen, M.: Synthesis of advanced ceramics in the systems Si-B-N and Si-B-N-C employing novel precursor compounds, *Mater. Res. Soc. Symp. Proc.*, **271**, 821-826, (1992).
- Baldus, P., Jansen, M., Sporn, D.: Ceramic fibers for matrix composites in high-temperature engine applications, *Science*, **285**, 699-703, (1999).
- Baldus, H.-P., Jansen, M.: Novel high-performance ceramics – amorphous networks from molecular precursors, *Angew. Chem., Int. Ed. Engl.*, **36**, 328-343, (1997).
- Riedel, R., Kienzle, A., Dressler, W., Ruwisch, L., Bill, J., Aldinger, F.: A silicoboron carbonitride ceramic stable to 2000 °C, *Nature*, **382**, 796-798, (1996).
- Jansen, M., Jäschke, B., Jäschke, T.: Amorphous multinary ceramics in the Si-B-N-C system, *Struct. Bonding*, **101**, 137-191, (2002).
- Jäschke, T., Jansen, M.: Improved durability of Si/B/N/C random inorganic networks, *J. Eur. Ceram. Soc.*, **25**, 211-220, (2005).
- Jäschke, T., Jansen, M.: A new borazine-type single source precursor for Si/B/N/C ceramics, *J. Mater. Chem.*, **16**, 2792-2799, (2006).
- Haberecht, J., Krumeich, F., Grützmacher, H., Nesper, R.: High-yield molecular borazine precursors for Si-B-N-C ceramics, *Chem. Mater.*, **16**, 418-423, (2004).
- Haberecht, J., Nesper, R., Grützmacher, H.: A construction kit for Si-B-N-C ceramic materials based on borazine precursors, *Chem. Mater.*, **17**, 2340-2347, (2005).
- Schurz, F., Jansen, M.: Borazine based molecular single source precursors for Si/B/N/C ceramics, *Z. Anorg. Allg. Chem.*, **636**, 1199-1205, (2010).
- Roth, A., Jansen, M.: Silicon Borocarbonitride Ceramics from Polycyclic Precursor Compounds, Processes for Producing Them and Use, (in German), German Patent Application *DE 10 2006 013 469 A1*, (2006).
- Epple, A.: Synthesis and Characterization of New Single-Source Precursors and Ceramics in the Si/B/N/C System and Solid-State NMR Investigations of Isotope-Labelled SiBN₃C, (in German), *Ph.D. thesis*, University of Stuttgart, (2006).

- ¹³ Cakmak, H., Jansen, M.: Synthesis and characterization of a new silaborazine derivative, *Z. Anorg. Allg. Chem.*, **637**, 25-28, (2011).
- ¹⁴ Wilfert, J., Meier, K., Hahn, K., Grin, Y., Jansen, M.: SiC/BN composites by spark plasma sintering (SPS) of precursor-derived SiBNC powders, *J. Ceram. Sci. Tech.*, **1**, 1-6, (2010).
- ¹⁵ Nöth, H., Tinhof, W., Taeger, T.: Silaborazines Derived from Cyclosilazanes, (in German), *Chem. Ber.*, **107**, 3113-3120, (1974).
- ¹⁶ Kroschel, M.: Amorphous B/Si/C/N-High-Performance Ceramics Derived from Single-Source Precursors, (in German), *Ph.D. thesis*, University of Bonn, (2001).

