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Boron-modified poly(propenylsilazane)-derived Si–B–C–N ceramics: preparation and high temperature properties

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Dedicated to Professor Günter Petzow on the occasion of his 75th birthday

Abstract

Boron-modified poly(propenylsilazanes) $[B\{C_3H_6Si(CH_3)NH\}_3]_n$ are synthesized via both ammonolysis of $B(C_3H_6Si(CH_3)Cl_2)_3$ (monomer route) and hydroboration of $[(H_2C{=}CHCH_2)Si(CH_3)NH]_n$ ($n = 3, 4$) (polymer route) and subsequently transformed into ceramic materials by pyrolysis up to 1400 °C. Thermogravimetric analysis of the as-obtained materials as well as X-ray diffraction of annealed samples were performed to investigate high temperature properties, revealing the stability of the materials toward thermal degradation up to 1800 °C and the presence of silicon nitride at 1800/2000 °C. The crystallization is additionally investigated by transmission electron microscopy. SiC crystallization is observed first, followed by the evolution of a composite material which is composed of a turbostratic BNC matrix embedding SiC and Si_3N_4 nanocrystals. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Electron microscopy; Precursors-metallorganic; Si–B–C–N; Thermal properties

1. Introduction

One of the most striking features of many precursor-derived Si–B–C–N ceramics over binary and ternary compositions is their remarkably high resistance toward thermally induced degradation or decomposition even at very high temperatures.[1–3] The onset of decomposition in these boron-containing materials is frequently shifted to temperatures of approximately 2000 °C. Thermally induced degradation is usually due to evaporation of nitrogen generated by decomposition of silicon nitride which is present in all these materials. In many Si–B–C–N ceramics the reaction is efficiently hindered, permitting temporary mass stability at elevated temperatures. According to thermodynamic calculations the decomposition of Si_3N_4 into the elements should start at about 1840 °C [1 atm N_2, Eq. (1)]; in the presence of carbon, decomposition according to Eq. (2) is expected at even lower temperature (1480 °C, 1 atm N_2).[4]

$$Si_3N_4 \rightarrow 3\,Si + 2N_2\uparrow \qquad (1)$$

$$Si_3N_4 + 3\,C \rightarrow 3\,SiC + 2N_2\uparrow \qquad (2)$$

The models that were developed to explain the unusual thermal stability of Si–B–C–N ceramics are based on microstructural investigations using (high resolution) transmission electron microscopy [(HR)TEM], chemical analysis and thermodynamic calculations.[4–10] Even though it is supposed that mainly the Si_3N_4 and BN phase fractions play an important role, there is still need to go into more detail. In order to gain more insight into the structural evolution, we describe here a new precursor system providing high temperature stable ceramic materials which were analyzed by thermogravimetric analysis, XRD, and (HR)TEM.

2. Experimental section

2.1. General comments

All reactions were carried out in a purified argon atmosphere using standard Schlenk techniques.[11]

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Allyldichloromethylsilane ($H_2C{=}CHCH_2)Si(CH_3)Cl_2$ was obtained from Sigma-Aldrich GmbH, Germany, and freshly distilled before use. Borane dimethylsulfide (2 M solution in toluene) was obtained from Sigma-Aldrich. Tetrahydrofurane and toluene were purified by distillation from potassium.

Fourier transform infrared spectra were obtained with a Bruker IFS66 spectrometer as KBr pellets (solids) or as films in NaCl cells (liquids). ^1H, ^{13}C, and ^{29}Si-NMR spectra in solution were recorded on a Bruker Avance 250 spectrometer operating at 250.07, 62.89, and 49.68 MHz, respectively. Chemical shifts are reported in δ relative from tetramethylsilane ($\delta=0$) with the solvent as an internal standard.

Chemical analysis was performed using a combination of different analysis equipment (ELEMENTAR Vario EL, ELTRA CS 800 C/S Determinator, LECO TC-436 N/O Determinator) and by atom emission spectrometry (ISA JOBIN YVON JY70 Plus). Thermogravimetric analysis (TGA) of the polymer-to-ceramic conversion was carried out in a flowing argon atmosphere (100 cm^3/min) with Netzsch STA 409 equipment (25–1400 °C, heating rate 5 °C/min) in alumina crucibles.

Pyrolysis of bulk preceramic materials was carried out in Al_2O_3 Schlenk tubes in a flowing argon atmosphere (heating rate 25–1400 °C: 1 °C/min followed by a dwell time of 2 h).

High temperature thermogravimetric analysis (HT-TGA) of the as-obtained ceramic samples operating a Netzsch STA 501 equipment was carried out in an argon atmosphere (25–2150 °C; heating rate $T<1400$ °C: 10 °C/min, $T>1400$ °C: 5 °C/min) using carbon crucibles. Crystallization of as-obtained ceramics was performed in graphite furnaces using graphite crucibles (heating rate $T<1400$ °C: 10 °C/min, $T>1400$ °C: 2 °C/min, dwell time 5 h) in an argon atmosphere. The X-ray diffraction unit used for structural investigations of the annealed samples was a Siemens D5000/Kristalloflex (Cu-$K_{\alpha1}$ radiation), equipped with an OED and a quartz primary monochromator. Samples were powdered in a WC ball mill prior to analysis. Mass spectrum–coupled gas chromatography (GC–MS) was performed using a Hewlett Packard 5890 Series II for GC (column HP-5MS 30 $m\times0.25$ mm, phase thickness 0.25 μm, carrier gas helium 0.066 ml/min) and a Finnigan MAT 95 for MS at the Institut für Organische Chemie der Universität Stuttgart. The sample was ionized by chemical ionization (CI, reactand gas CH_4).

TEM specimens were prepared by polishing and dimpling. In the case of brittle and porous samples or single ceramic particles, alumina cross section holders were used to stabilize the sample material during the preparation steps. This technique was developed by Strecker et al.[12] The final thinning to electron transparency was performed by Ar ion beam bombardment in a Baltec Res 010 at an angle of 6° and an ion energy of 5 keV.

Elemental distribution and bright field images were taken in an energy filtering transmission electron microscope (EFTEM) Zeiss EM 912 Omega operating at 120 kV. The instrument is equipped with an imaging omega filter. The ‘three window method’ [13] was applied to obtain the elemental distribution images: two images are taken in the structureless background of the electron energy loss (EEL) spectrum. Using these two images, the background can be extrapolated and subtracted from a third image which is acquired above the edge and contains the element specific signal. Quantitative information about the local chemical composition of the ceramics was gathered by acquiring EEL-spectra between 50 and 450 eV. In this energy range the silicon L-edge (99 eV), the boron K-edge (188 eV), the carbon K-edge (284 eV), and the nitrogen K-edge (401 eV) are present. The spectra were evaluated with the Gatan EL/P 3.0 software.

Electron diffraction images were zero loss filtered to remove the disturbing inelastic background.[14]

The HRTEM investigations were performed using a Jeol 4000 EX operating at 400 kV.

2.2. *Synthesis of the precursors*

2.2.1. *Synthesis of $B[(C_3H_6)Si(CH_3)Cl_2]_3$ (**1**)*[15]

To a solution of 78.55 g ($H_2C{=}CHCH_2)Si(CH_3)Cl_2$ (506 mmol) in 120 ml toluene, 85 ml of a 2 M solution of $H_3B{\cdot}SMe_2$ (169 mmol) in toluene were added dropwise at 0 °C under vigorous stirring. The reaction mixture was allowed to warm overnight to room temperature. After evaporation of the solvent and SMe_2 under reduced pressure, the title compound was dried in vacuum at 40 °C. The chemical yield of the colorless oily product was 80.94 g (100%).

Chemical analysis **(1)** $[BSi_3C_{12}H_{27}Cl_6]$ M = 479.13 g/mol, found (calcd wt.%): C 31.4 (30.1), H 5.1 (5.7), Si 17.6 (17.6), Cl 41.2 (44.4), B 2.4 (2.3), O 2.3 (0.0) $[BSi_{2.8}C_{11.8}H_{22.8}Cl_{5.2}O_{0.6}]$ IR (neat): 2929 *s* (ν C–H), 2870 *m* (ν C–H), 1561 *s*, 1454 *w* (δ_a C–CH_x), 1402 *m* (δ_s C–CH_x), 1343 *m*, 1261 *s* (δ $SiCH_3$), 1178 *m*, 980 *w* (ν C–C), 812 *s* (ρ CH_3Si), 788 *vs* (ρ CH_3Si), 746 *s* (ρ CH_3Si), 701 *m*, 537 *vs* (ν Si–Cl), 478 *s*.

2.2.2. *Synthesis of $[B\{(C_3H_6)Si(CH_3)NH\}_3]_n$ (**2a, 2b**)*

(a) In a 4 l Schlenk flask with a gas inlet tube, a mechanical stirrer, an inside thermometer and a water-cooled reflux condenser, 106.5 g of **1** (227 mmol) were dissolved in 1.5 l of toluene. Under vigorous stirring, a moderate stream of ammonia was introduced, whereby a colloidal precipitate formed immediately. The temperature raised up to 65 °C. The reaction was complete after about 12 h. The mixture was filtered at room temperature several times through a pad of celite. The complete separation of insoluble products was not possible. The cloudy filtrate was concentrated and dried in vacuum at 70 °C to produce 13.1 g of a colorless, opaque, very gluey material **2a**. Chemical analysis revealed the contamination of the polymer with a significant amount of chlorine-containing species.

Chemical analysis **(2a)** $[Si_3C_{12}H_{30}N_3B]_n$ M = 311.46 g/mol, found (calcd, wt.%): C 41.2 (46.3), H 8.9 (9.7), N 11.5 (13.5), Si 20.9 (27.1), B 3.4 (3.5), Cl 9.9 (0.0), O 2.6 (0.0) $[Si_3C_{13.8}H_{35.6}N_{3.3}B_{1.27}Cl_{1.1}O_{0.7}]$.

(b) The processing parameters for the preparation of **2a** were changed in the following manner to synthesize **2b**: solvent: THF, reaction temperature: 0–5 °C, apparatus equipped with a dry ice/isopropanol reflux condenser, reaction time: 3 h, until liquid ammonia condensed in the reflux condenser.

Again the precipitate was very close-grained and could not be separated by filtration. Therefore, the reaction mixture was dried completely in vacuum at room temperature to produce a colorless, non-sticky powder. After addition of 1.5 l of toluene and heating to reflux for 3 h, the hot mixture was filtered. The clear solution was concentrated in vacuum at 40 °C to produce a yellow oil, which was dried in vacuum at 70 °C. Yield: 5.0 g (7%) of **2b**, which contains only a small amount of chlorine.

Chemical analysis **(2b)** $[Si_3C_{12}H_{30}N_3B]_n$ M = 311.46 g/mol, found (calcd wt.%): C 46.0 (46.3), H 9.6 (9.7), N 12.9 (13.5), Si 24.1 (27.1), B 3.5 (3.5), Cl 1.1 (0.0), O 1.8 (0.0) $[Si_3C_{13.4}H_{33.3}N_{3.2}B_{1.13}Cl_{0.1}O_{0.4}]_n$.

IR (KBr): 3404 *m*, *br* (ν N–H), 2969 *m* (ν C–H), 2920 *m* (ν C–H), 2848 *m* (ν C–H), 1254 *s* (δ_s C–CH_x), 1159 *m* (δ SiNH), 927 *s* (ν Si–N), 795 *s* (ρ CH_3Si).

*2.2.3. Synthesis of $[(H_2C{=}CHCH_2)Si(CH_3)NH]_n$ (**3**)*[16]

The ammonolysis reaction was carried out as described for the synthesis of **2b**. In contrast to the procedure described in the literature,[16] THF was used instead of benzene and the temperature of the reaction mixture was 0–5 °C.

116.5 g $(H_2C{=}CHCH_2)Si(CH_3)Cl_2$ (750 mmol) in 1 l THF, reaction time 1.5 h.

After filtration, the precipitate was extracted two times. The combined solutions were concentrated in vacuum at room temperature. The residue was dried in vacuum at room temperature (5×10^{-2} mbar) to yield 61.73 g (83%) of the colorless, low-viscous oil **3**.

Chemical analysis **(3)** $[SiC_4H_9N]$ M = 99.21 g/mol, found (calcd wt.%): C 48.1 (48.4), H 8.6 (9.1), N 14.3 (14.1), Si 27.1 (28.3), O 1.5 (0.0) $[SiC_{4.2}H_{8.8}N_{1.1}O_{0.1}]$.

IR (neat): 3386 *m*, *br* (ν N–H), 3076 *m* (ν =C–H), 2969 *m* (ν C–H), 1629 *m* (ν C=C), 1420 *w* (δ_{as} C–CH_x), 1253 *s* (δ_s C–CH_x), 1177 *vs* (δ SiNH), 1033 *m* (ν C–C), 993 *w* (ν C–C), 926 *vs* (ν Si–N), 894 *s*, 796 *s* (ρ CH_3Si), 573 *m*.

^1H NMR (C_6D_6): $\delta = 0.14$ (*s*, 3H, CH_3), 0.38 (*s*, *br*, 1H, N*H*), 1.60 (*t*, $^3J = 8.1$, 2H, $SiCH_2$), 4.98–5.05 (*m*, 2H, $=CH_2$), 5.81–6.00 (*m*, 1H, =C*H*).

^{13}C: $\delta = 2.24$ ($SiCH_3$), 29.31 ($SiCH_2$), 113.33 ($=CH_2$), 135.62 (=*C*H).

^{29}Si: trimer: −6.82, −6.99, −7.07; tetramer: −9.98, −10.11, −10.20, −10.27.

GC–MS [M=$(C_3H_5)Si(CH_3)NH$]: peak 1 (trimer, retention time 18.0 min, integral 4393274): *m/z* 298 (3% M_3+H^+), 282 (5% $M_3^+{-}CH_3$), 256 (100% $M_3^+{-}C_3H_5$), 239 (4% $M_3^+{-}C_3H_5{-}CH_3{-}2H$), 214 (37% $M_3^+{-}2\ C_3H_5{-}H$), 197 (1% $M_3^+{-}2\ C_3H_5{-}CH_3{-}3H$), 174 (1% $M_3^+{-}3\ C_3H_5$); peak 2 (tetramer, retention time 22.6 min, integral 1097869): *m/z* 397 (4% M_4+H^+), 381 (5% $M_4^+-CH_3$), 355 (100% $M_4^+-C_3H_5$), 313 (9% $M_4^+-2\ C_3H_5-H$), 296 (6% M_3^+-H), 271 (17% $M_4^+-3\ C_3H_5-2H$)

*2.2.4. Synthesis of $[B\{(C_3H_6)Si(CH_3)NH\}_3]_n$ (**4**)*

To a solution of 18.92 g of **3** (191 mmol) in 200 ml of toluene, 31.8 ml of a 2M solution of $H_3B{\cdot}SMe_2$ (64 mmol) in toluene were added dropwise under vigorous stirring at 0 °C. After warming up to room temperature and stirring for an additional hour, the viscosity of the reaction mixture started to increase to give a colorless gel. After 12 h the volatile compounds were evaporated in vacuum at 60 °C to produce 19.7 g (63.3 mmol, 100%) of solid **4**.

Chemical analysis **(4)** $[BSi_3C_{12}H_{30}N_3]_n$ M = 311.46 g/mol, found (calcd wt.%): C 46.5 (46.3), H 9.6 (9.7), N 14.3 (13.5), Si 24.2 (27.1), B 3.5 (3.5), O 0.8 (0.0) $[Si_3C_{13.5}H_{33.2}N_{3.6}B_{1.13}]$ IR (KBr): see data of **2b**.

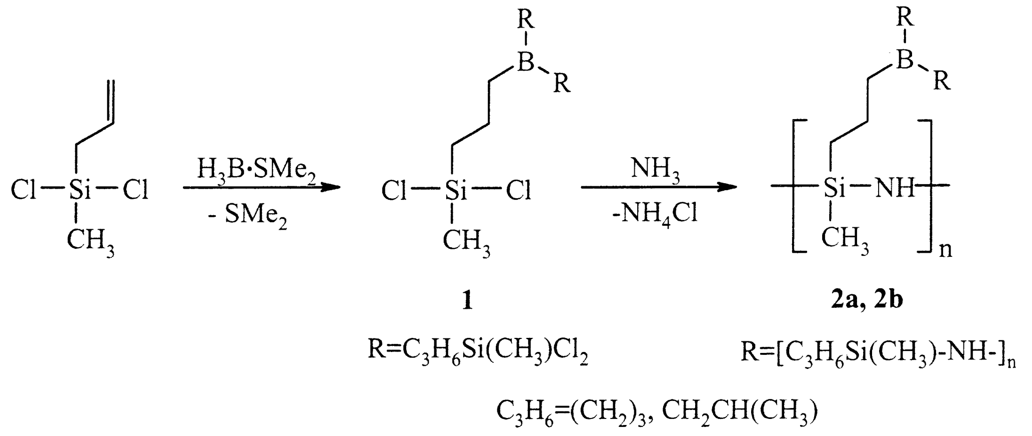
3. Results and discussion

3.1. Polymer synthesis

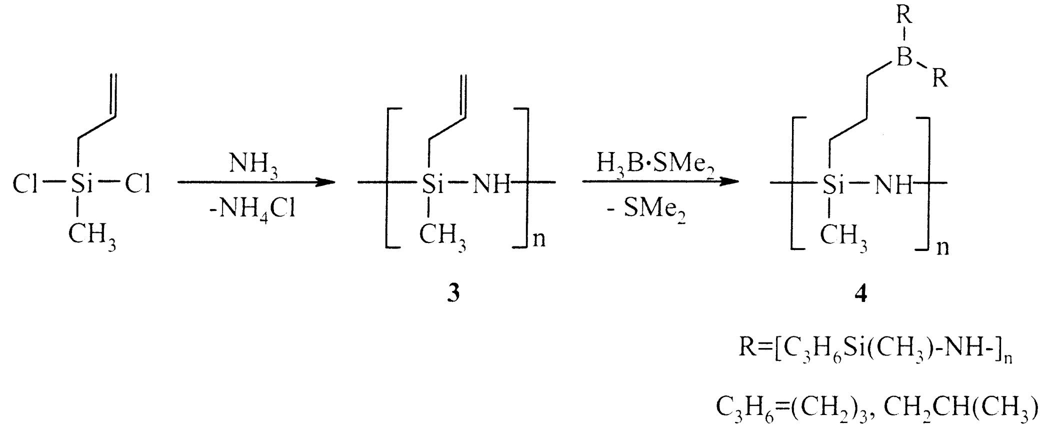
Polymeric Si–B–C–N precursors of the general type $[B(C_xH_{2x}SiRNR')_3]_n$ ($x = 2, 3\ldots$) can be synthesized by two different reaction pathways [Eqs. (3 and 4)]. Starting with allyldichloromethylsilane, $(H_2C{=}CHCH_2)Si(CH_3)Cl_2$, as the monomeric silicon/carbon source, polyborosilazanes **2** and **4** were obtained. Following the monomer route, the silane is first reacted with borane dimethylsulfide and subsequently treated with ammonia [Eq. (3)] to yield boron-modified polysilazane **2**. The reaction sequence can also be inverted. The ammonolysis of allyldichloromethylsilane yields liquid oligosilazanes **3** which can more easily be separated from solid products than **2**. Subsequent hydroboration of the alkenyl groups with borane dimethylsulfide produces **4** [polymer route, Eq. (4)].

3.1.1. Monomer route

The exothermic reaction of $(H_2C{=}CH{-}CH_2)Si(CH_3)Cl_2$ and $H_3B{\cdot}SMe_2$ yields moisture and air-sensitive tris(dichloromethylsilylpropyl)borane **1** as a colorless liquid. The IR and NMR spectra of the product show no signals of unreacted allyl side chains or B–H containing by-products indicating complete addition of the borane to the C=C double bond.



(3)



(4)

Both ^{1}H and ^{13}C NMR spectra of compound **1** are very complex and will not be discussed here in detail. The appearance of such complex spectra is known from silyl-ethylboranes that were obtained by hydroboration of vinylsilanes with $H_3B{\cdot}SMe_2$. A mixture of different regio- (α- and β-addition products) and stereoisomers is produced in this reaction.[17] However, Jones and Myers, who in 1972 investigated the hydroboration of allyldichloromethylsilane with diborane, only found the anti-Markovnikov addition product.[15] We thus conclude that the regioselectivity of the hydroboration possibly depends on the reaction conditions and the borane source.

Subsequent ammonolysis of **1** was performed in toluene solution at room temperature (**2a**) or in THF at 0 °C (**2b**). In both cases, the products partly remained colloidal in solution. A thorough separation of ammoniumchloride by filtration was not possible. The efforts made to purify **2b** (hot extraction of the dried reaction mixture with toluene) had a limited success, since the chlorine content was still at 1.1 wt.%. Moreover, the chemical yield was very poor (7%). Consequently, this method is not suitable for the synthesis of large amounts of pure **2**.

3.1.2. Polymer route

Ammonolysis of allyldichloromethylsilane was first carried out by D. Ya. Zhinkin et al. in 1963 [16] by reaction with gaseous ammonia in benzene at 30 °C. They isolated silazane-rings in 74% yield. With changed reaction conditions (0 °C in THF) we obtained a colorless liquid product, $[(H_2C{=}CHCH_2)Si(CH_3)NH]_n$ (**3**), in 83% yield which was characterized by IR and NMR spectroscopy (see Experimental). In the ^{29}Si NMR spectrum two distinct sets of signals are observed centered at −7.16 and −10.06 ppm, respectively, which can be assigned to silicon atoms bound in six- and eight-membered silazane rings.[18,19] Mass spectrum-coupled gas chromatography revealed that the reaction produces a 4:1 mixture of trimers and tetramers.

The hydroboration of oligo(allylmethyl)silazane **3** with borane dimethylsulfide was performed in toluene at 0 °C. After complete addition of $H_3B{\cdot}SMe_2$ and additional stirring for 1 h, a sol-gel transformation was observed. The polymer **4** was dried to yield 100% of a colorless, glass-like material. The absence of $H_2C{=}CH$ vibration bands in the IR spectrum shows that the allyl group has completely reacted.

3.2. Pyrolysis

The polymers **2a**, **2b**, and **4** were pyrolysed at 1400 °C in a flowing argon atmosphere to produce the ceramic materials **2a–c**, **2b–c** and **4c**. The mass loss during the transformation of **2b** and **4** was determined by thermogravimetric analysis (see Fig. 1).

The decomposition behavior of the two polymers is very similar. In both cases, one single mass loss step is observed between about 250 and 500 °C leading to a final ceramic yield of about 20% at 1400 °C. The mass loss of **4** is with 78.4% slightly smaller than that of **2b** with 82.2%, which can be a consequence of the NH_4Cl contamination of **2b**. The very poor yield indicates that depolymerization and volatilization of smaller molecules occur.

The colorless polymers are transformed into hard black ceramic materials the composition of which is given in Table 1. Chemical analysis revealed the complete burn out of ammonium chloride. The atomic ratios found for the three materials are very similar. As main differences, the boron content is slightly decreased in **4c**, whereas the nitrogen content is increased.

3.3. High temperature thermogravimetric analysis (HT–TGA)

The thermal stability of the as-pyrolysed ceramics was determined by HT–TGA. The samples were gradually heated to 2150 °C in an argon atmosphere while the mass change was detected. The results of the HT–TGA of **2a–c**, **2b–c**, and **4c** are shown in Fig. 2. For comparison, the data of the ceramic material **T2/1c** derived from the polymer **T2/1**, known from the literature,[2] are added.

Up to 1800 °C the sample masses of the materials investigated do not change significantly. Further increasing the temperature to 1900 °C leads to a slight mass loss of 0.2% for material **4c**, 0.6% for **T2/1c**, 1.1% for **2a–c** and 1.3% for **2b–c**. At 2000 °C the mass loss of **4c** does not exceed 0.6% whereas the decomposition of **T2/1c**, **2a–c**, and **2b–c** is clearly accelerated. Further mass loss at higher temperatures proceeds very fast for materials **2a–c** and **2b–c** to attain a final value of 14.5 and 10.6% at 2150 °C, respectively. The negative slope of the curve of material **4c** is clearly smaller. At 2150 °C, the mass loss comes to 1.6% for **4c**, compared to **T2/1c** with a mass loss of 5.6%.

Table 1
Chemical compositions of as-pyrolysed ceramic materials **2a–c**, **2b–c**, and **4c** (wt.%)

Compound	Si	C	N	B	O	Formula
2a–c	37.6	33.9	17.6	6.1	3.4	$[B_9Si_{22}C_{47}N_{21}(O_3)]$
2b–c	36.0	35.1	17.0	6.4	3.9	$[B_{10}Si_{21}C_{49}N_{20}(O_4)]$
4c	41.0	32.4	19.6	5.1	0.9	$[B_8Si_{24}C_{45}N_{23}(O_1)]$

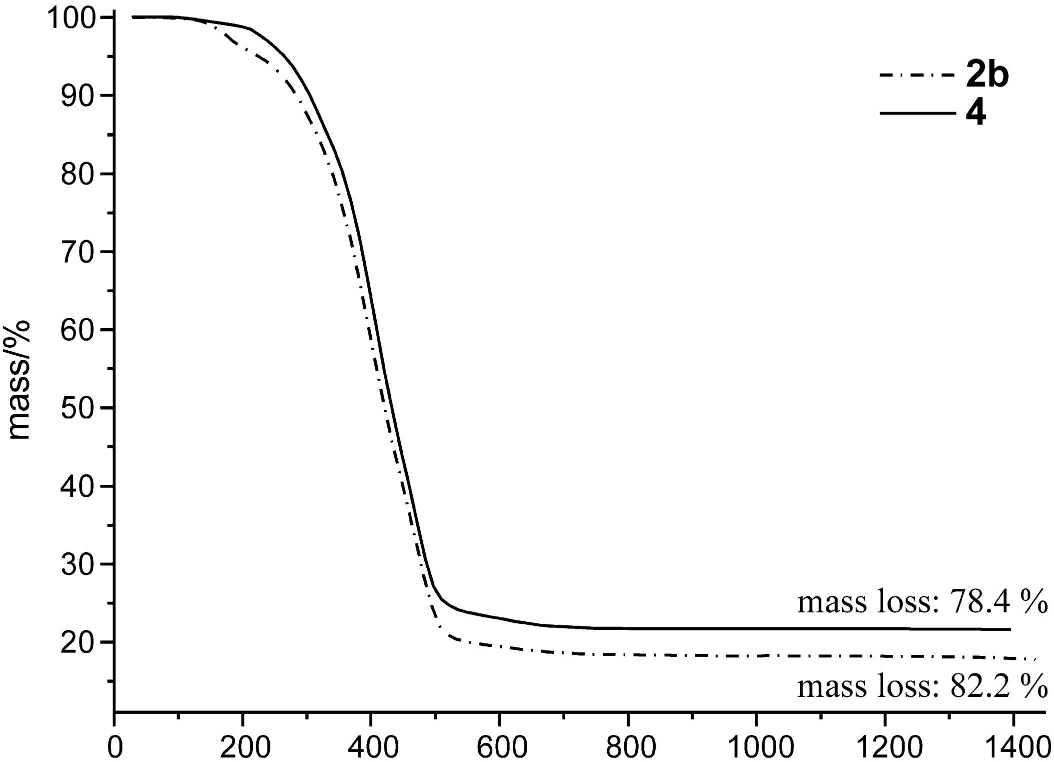


Fig. 1. Thermogravimetric analysis of the polymer-to-ceramic transformation of **2b** and **4** (heating rate 5 °C/min, argon atmosphere).

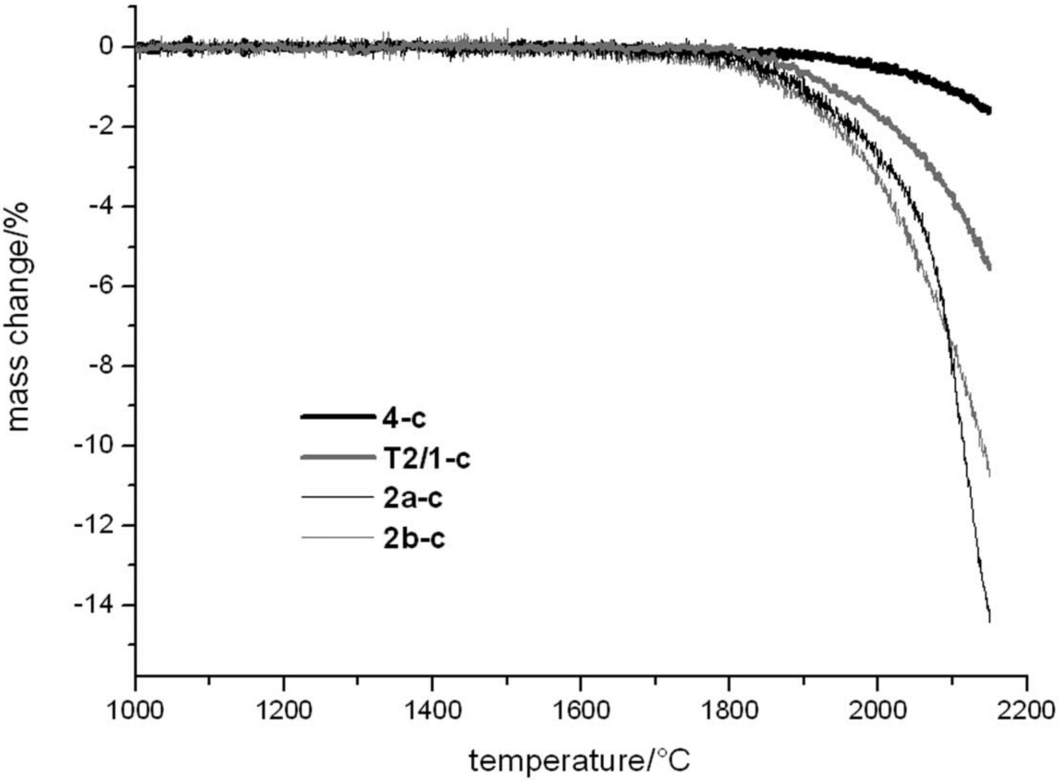


Fig. 2. HT–TGA of **T2/1c**, **2a–c**, **2b–c**, and **4c** (1000–2150 °C, Ar atmosphere).

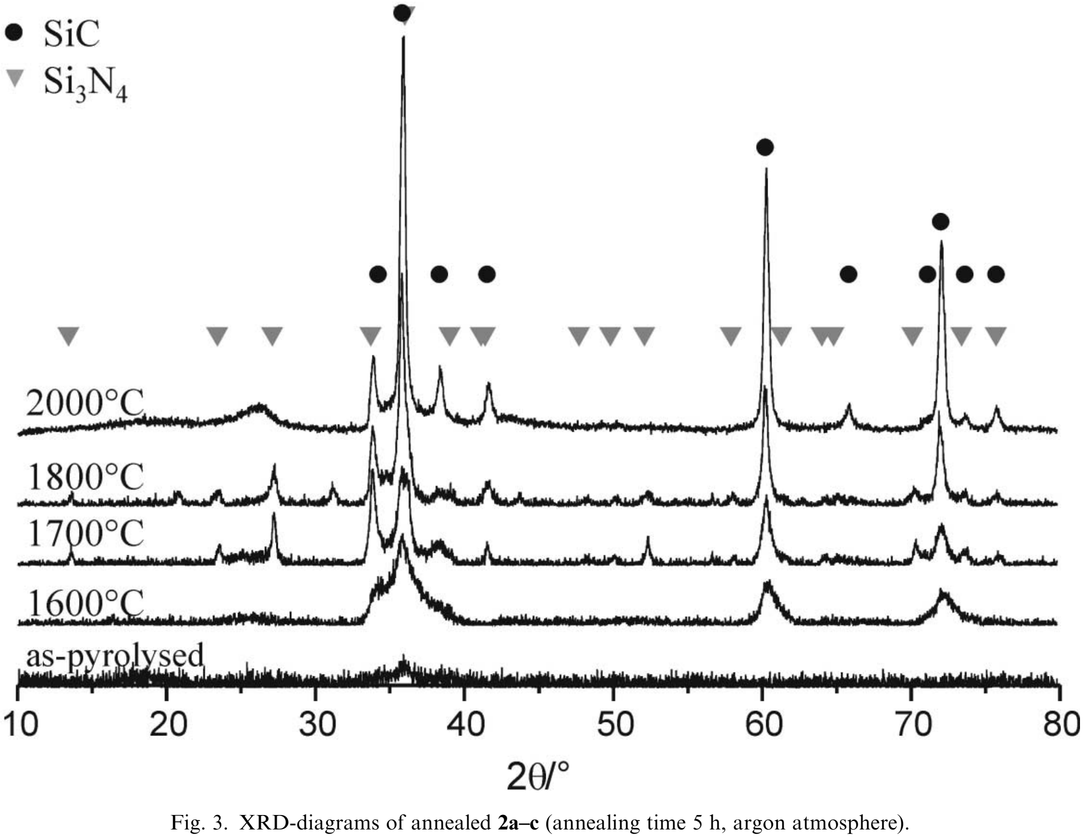


Fig. 3. XRD-diagrams of annealed **2a–c** (annealing time 5 h, argon atmosphere).

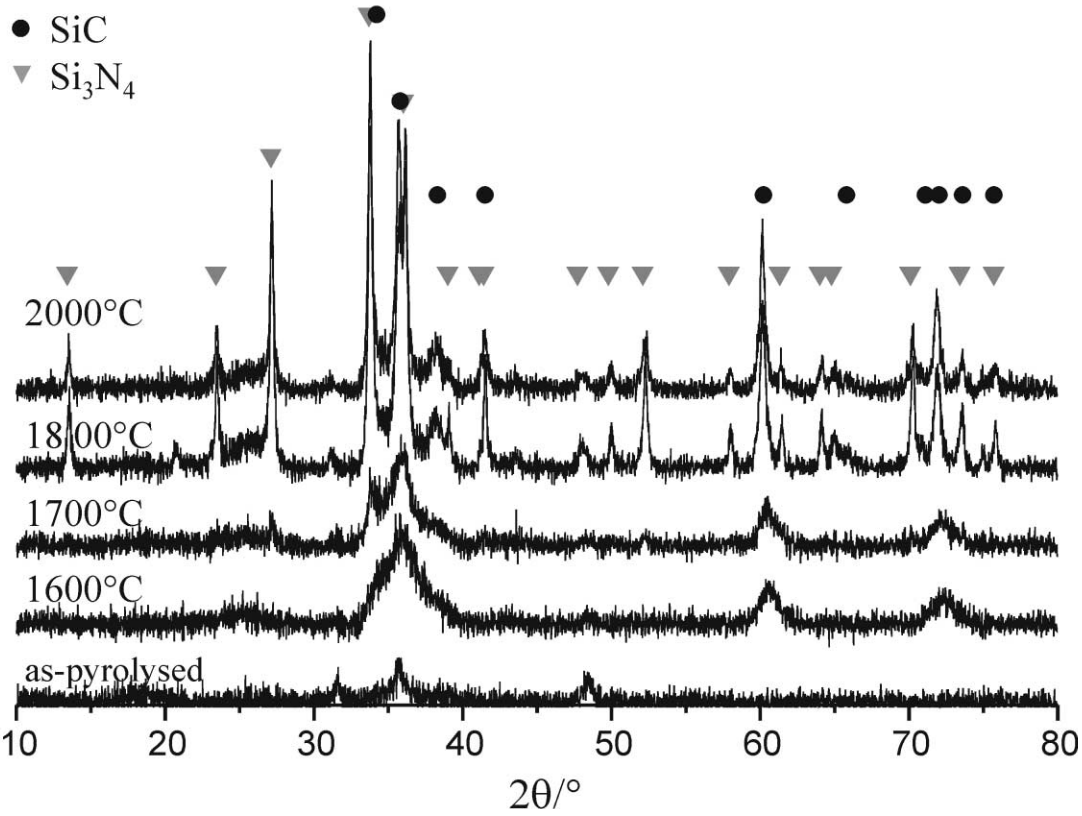


Fig. 4. XRD-diagrams of annealed **4c** (annealing time 5 h, argon atmosphere).

3.4. X-ray diffraction

To study the crystallization behavior, the materials **2a–c** and **4c** were annealed at different temperatures for 5 h each in an argon atmosphere and analyzed by X-ray diffraction (see Figs. 3 and 4).

The as-pyrolysed ceramics are X-ray amorphous. Crystallization starts at about 1600 °C for material **2a–c** (Fig. 3). Very broad reflections indicate the presence of small SiC crystals. At 1700 °C the line width decreases considerably. In addition to SiC reflections, signals of crystalline Si_3N_4 can clearly be detected. By further heating to 1800 °C, the line width is again reduced. The position and intensity of the peaks roughly remain constant. At 2000 °C finally, crystalline silicon nitride is completely decomposed. Besides silicon carbide reflections a very broad signal at about 26 ° is detected indicating the presence of graphite-like structures.

The crystallization behavior of **4c** is very similar up to 1600 °C (see Fig. 4). At 1700 °C however, the X-ray diffraction peaks are still very broad. In contrast to **2a–c**, silicon nitride reflections are very weak after heat treatment at this temperature. Only the Si_3N_4 reflection at 27.1° reveals the presence of this phase. The amount of crystalline Si_3N_4 increases significantly between 1700 and 1800 °C. Compared to the respective X-ray diagram of **2a–c**, the silicon nitride reflections after heat treatment at

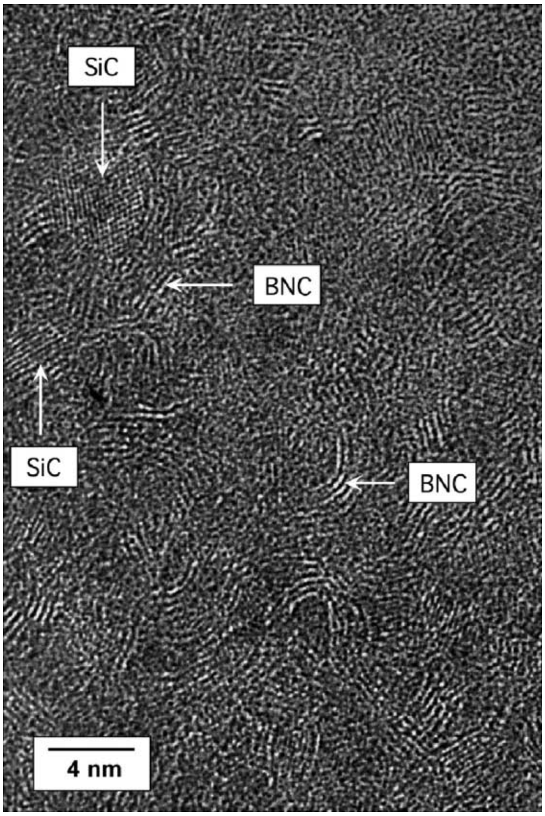


Fig. 5. HRTEM micrograph of as-pyrolysed **4c** with SiC crystallites and turbostratic layers.

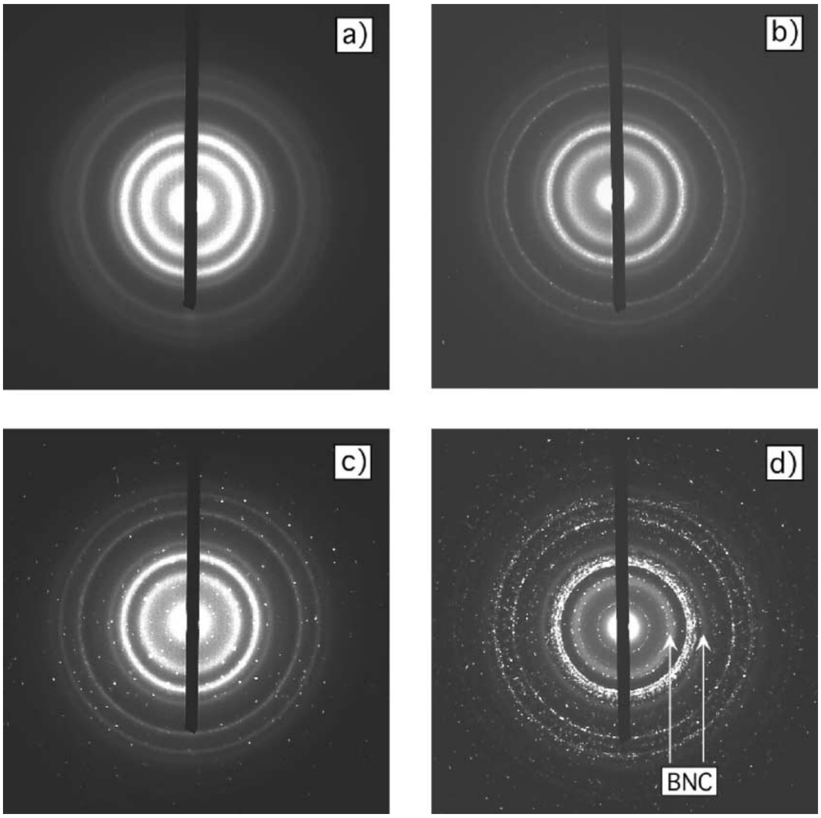


Fig. 6. Electron diffraction pattern of (a) as-pyrolysed and annealed **4c** (b) 1600 °C, (c) 1700 °C, (d) 1800 °C.

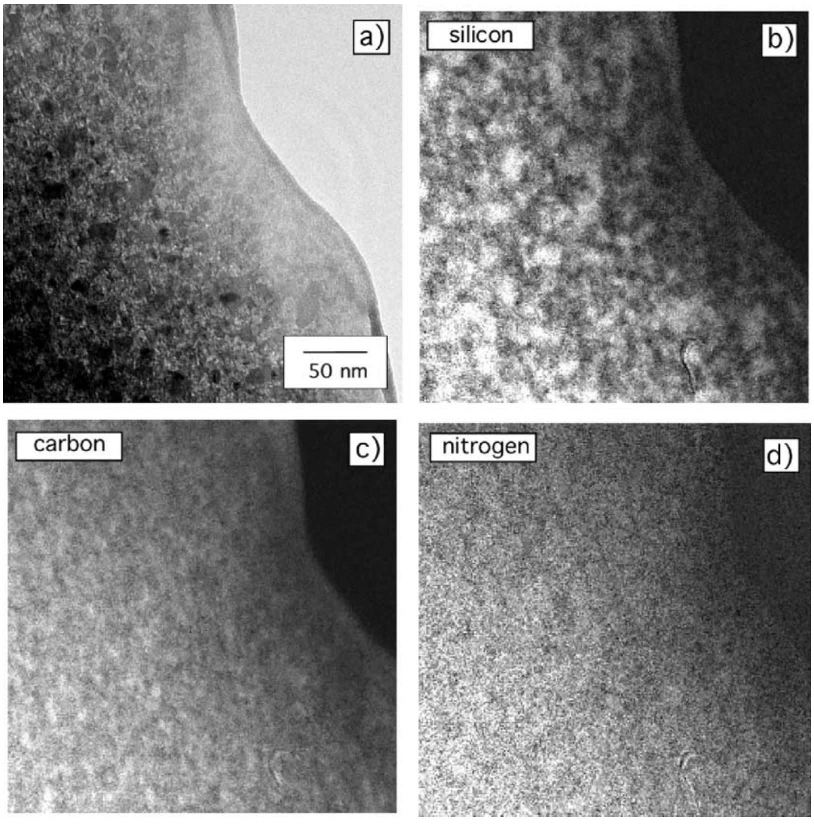


Fig. 7. (a) Bright field image and elemental distribution images of (b) Si, (c) C, (d) N of **4c** annealed at 1600 °C.

1800 °C are noticeably stronger. At 2000 °C finally, the position of the signals and their relative intensity remain nearly constant in comparison to the 1800 °C diffractogram, indicating the thermal stability of the crystalline phases Si_3N_4 and SiC present in the microstructure.

3.5. *Transmission electron microscopy*

Transmission electron microscopy (TEM) was performed to get more insight into the evolution of the microstructure of material **4c**. Information about grain size and homogeneity is obtained. The distribution of particular chemical elements is shown in elemental maps, where bright areas reveal the presence and dark areas the absence of a certain element. In addition energy-filtering TEM (EFTEM) was used to get knowledge about the local chemical composition of the material.

3.5.1. *As-pyrolysed sample*

Fig. 5 shows a HRTEM micrograph of the as-pyrolysed sample. The small crystallites with diameters of 2–4 nm were identified with their EDP (electron diffraction pattern) lattice parameters to be SiC. XRD measurements (Fig. 4) were not sensitive enough to detect this crystalline phase. In Fig. 5 turbostratic graphite-like structures are also denoted which are very similar to the BNC-matrix of the fully crystallized sample (annealed at 1800 °C, Fig. 10). These layers probably represent an early BNC phase. The EDP (Fig. 6a) shows reflections of crystalline SiC besides two broad diffuse rings which we assign to the BNC phase.

The formation of SiC within the as-pyrolysed sample is in accordance with the results on the ceramization behavior of boron-containing polysilazanes. Solid state NMR investigations of these polymers[20] revealed that the coordination number of silicon with respect to nitrogen decreases during pyrolysis because of the preferred formation of B–N bonds. As a consequence, the coordination-sphere of silicon becomes carbon-rich; pathways for the formation of SiC_4 units, an early stage of silicon carbide, are provided.

3.5.2. *1600 °C sample*

The bright field image of a sample annealed at 1600 °C (Fig. 7a) shows small grey areas with an average diameter of approximately 12 nm which correspond to the bright areas in the silicon distribution image (Fig. 7b). The silicon-poor areas are bright in the carbon image

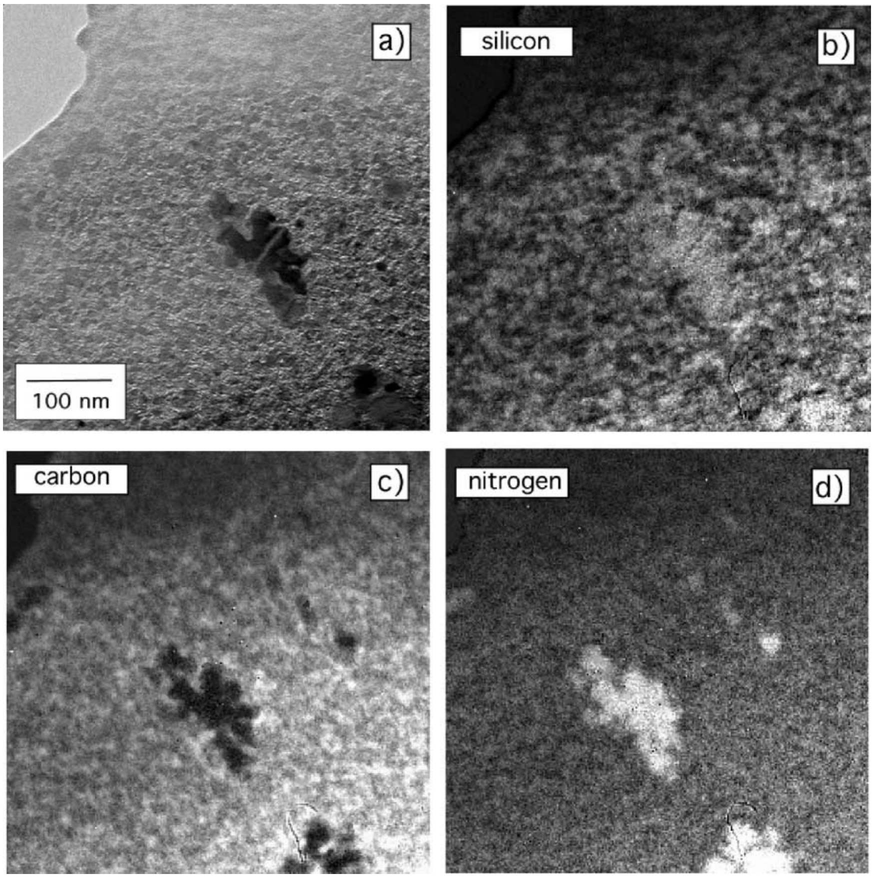


Fig. 8. (a) Bright field image and elemental distribution images of (b) Si, (c) C, (d) N of **4c** annealed at 1700 °C.

(Fig. 7c) because the carbon content is higher in the surrounding matrix than in silicon-rich islands.

The carbon-rich BNC phase already seems to be at least partially established in this early crystallization state. Nitrogen atoms (Fig. 7d) are located both in the silicon-containing and in the matrix phase. The EDP (Fig. 6b) is very similar to that of the as-pyrolysed sample, the reflections belonging to silicon carbide are more distinct, indicating growth of SiC crystals. The reflections assigned to the turbostratic BNC areas keep smooth.

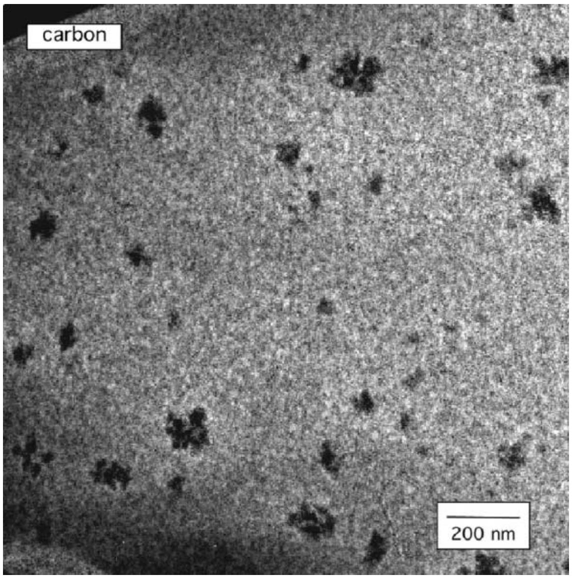


Fig. 9. Carbon distribution in **4c** annealed at 1700 °C.

3.5.3. 1700 °C sample

Fig. 8 shows the bright field image (a) and the elemental distribution images of a sample annealed at 1700 °C. The average diameter of the silicon-rich areas in the silicon distribution image (b)—exclusive of the larger silicon nitride crystals—is 16 nm. The Si_3N_4 crystals can be identified more clearly in the carbon map (c), where they appear as dark feature. The average diameter of these grain agglomerates is approximately 80 nm. They are composed of smaller grains with diameters of approx. 25 nm as was revealed by a carbon map taken at lower magnification (Fig. 9). They are not present in the 1800 °C sample (see Section 3.5.4). Their formation is probably due to the annealing conditions. Si_3N_4 grain growth seems to be favored compared to SiC grain growth. The EDP (Fig. 6c) clearly shows additional spots, indicating the presence of crystalline silicon nitride.

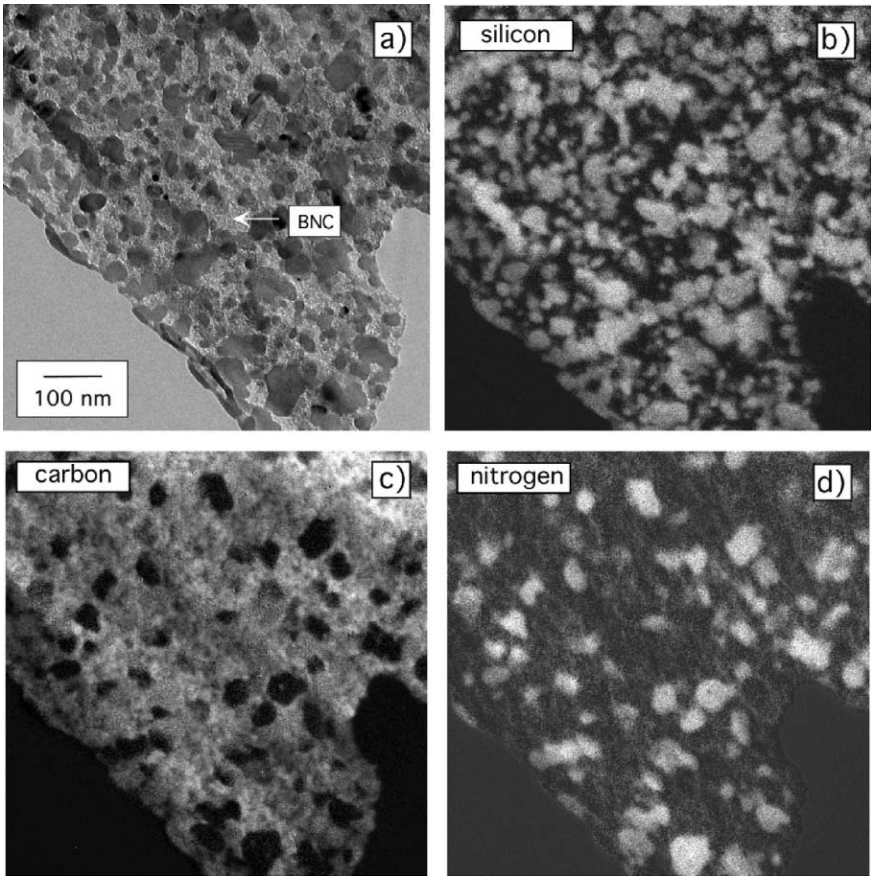


Fig. 10. (a) Bright field image and elemental distribution images of (b) Si, (c) C, (d) N of **4c** annealed at 1800 °C.

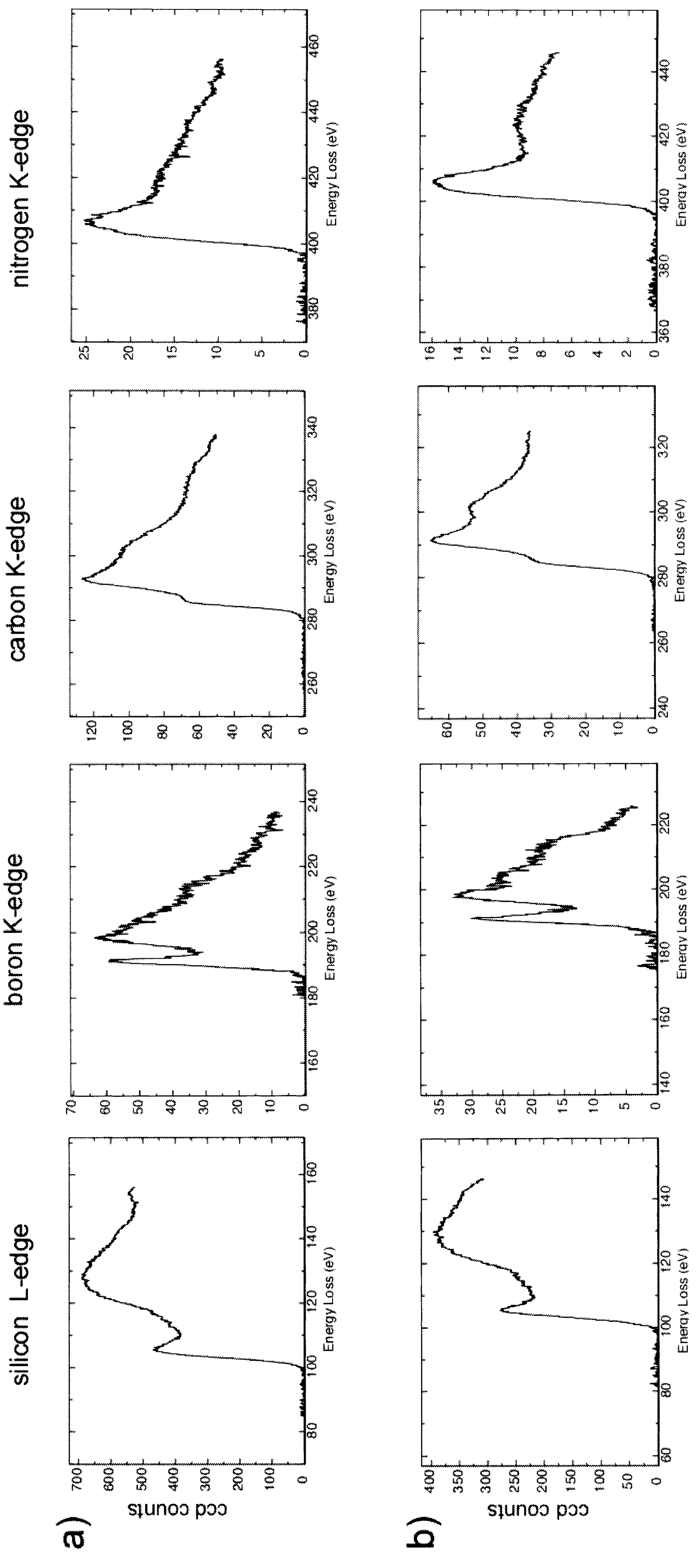


Fig. 11. EEL spectra of (a) as-pyrolysed and (b) annealed (1800 °C) **4c**.

3.5.4. 1800 °C sample

The sample annealed at 1800 °C consists of silicon nitride and silicon carbide crystals embedded in a turbostratic BNC-matrix (bright field image Fig. 10a). In the corresponding silicon map (Fig. 10b) the BNC-matrix appears dark whereas Si_3N_4 and SiC crystals are represented as bright areas. In the carbon map (Fig. 10c) silicon nitride appears dark, whereas SiC and BNC-matrix are bright. The nitrogen map (Fig. 10d) shows Si_3N_4 crystals as bright feature. The crystal size of SiC as well as Si_3N_4 is approx. 40 nm. The larger Si_3N_4 grain agglomerates found in the 1700 °C sample were not detected. The EDP shows reflections of silicon nitride and silicon carbide (Fig. 6d). The smooth reflections of the BNC matrix are indicated.

According to CALPHAD calculations (CALculation of PHAse Diagrams[21]) the relative amounts of thermodynamically stable phases present in a crystalline sample can be predicted. The composition determined by chemical analysis of the as-pyrolysed **sample 4c** is located in the phase field $BN+Si_3N_4+SiC+C$ (1400 °C, 1 bar N_2). The relative amounts of these phases are 15.8 at.% BN, 26.8 at.% Si_3N_4, 25.4 at.% SiC, and 32.0 at.% C.

These predictions can be compared to microstructural TEM results. In order to determine the overall chemical composition, quantitative EELS analysis was performed on the as-pyrolysed material (Fig. 11a) and the sample annealed at 1800 °C (Fig. 11b). EEL-spectra of the silicon L-edge, boron K-edge, carbon K-edge and nitrogen K-edge were recorded from a circular sample area with a diameter of 0.5 μm.

In the material pyrolysed at 1400 °C the atomic ratio of the elements Si:B:C:N was ca. 17:10:52:21 (quantitative evaluation of the spectra shown in Fig. 11a). In the 1800 °C sample it was estimated to be 17:10:51:22 (Fig. 11b). The uniformity of these two spectra series clearly shows that the sample composition has not changed significantly during the heat treatment. The EELS results differ from chemical analysis of the as-pyrolysed sample ($Si_{24}B_8C_{45}N_{23}$, see Experimental part and Table 1) mainly by the silicon content, whereas the relative B, C, and N contents are in good accordance within the error bars of this method (±15%). The systematic underestimation of the relative amount of silicon atoms is probably due to the difficulties bound up with the quantification of the silicon L-edge spectrum, whereas integration of the K-edge spectra of the lighter elements gives reasonable results.

Within the BNC-matrix of the crystalline material, EEL spectra were obtained from a filtered series of 33 images with energy steps of 10 eV between 120 and 440 eV in a 20×20 nm^2 area (Fig. 12). They revealed an atomic ratio of B:C:N of 1:4:1 which is exactly the value predicted by the CALPHAD approach of BN:C = 15.8:32. The "free carbon" must therefore be completely embedded in the turbostratic BNC layers. Reactions of C with silicon nitride [Eq. (2)] are hindered in this microstructure.

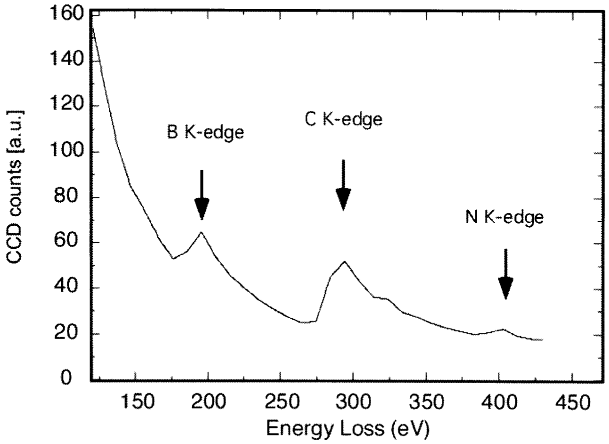


Fig. 12. EEL spectrum of the BNC matrix in **4c** annealed at 1800 °C.

4. Summary and conclusions

The boron-modified allylmethylsilazane $[B(C_3H_6Si(CH_3)NH)_3]_n$ was successfully prepared by hydroboration of oligoallylmethylsilazane (polymer route) whereas the product of ammonolysis of tris({dichloromethyl propyl}silyl)borane (monomer route) was contaminated with ammonium chloride. The products of these different routes were pyrolysed at 1400 °C to yield Si–B–C–N ceramics with very similar compositions. The polymer obtained by the polymer route delivered a material stable up to 2000 °C, whereas the material derived from the monomer route polymer decomposed at temperatures above 1800 °C. Up to 2000 or 1800 °C, the compositions of the materials were constant and the phase evolution could be predicted by thermodynamic calculations.

After pyrolysis, the samples were X-ray amorphous. (HR)TEM revealed the presence of 2–4 nm SiC crystals in an amorphous turbostratic matrix. Between 1400 and 1600 °C, no distinct evolution of the microstructure was observed. Only the size of SiC grains increased. Silicon nitride crystals were found in samples heat treated at 1700 °C. Formation and growth of Si_3N_4 was favored at this temperature in comparison with SiC. Samples annealed at 1800 °C consisted of crystalline SiC and Si_3N_4 in a turbostratic BNC matrix. After annealing for 5 h at 2000 °C, crystalline silicon nitride was detected in the ceramic material derived from the polymer route precursor, whereas it was absent in the ceramic sample obtained by the monomer route polymer.

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