A Construction Kit for Si−B−C−N Ceramic Materials Based on Borazine Precursors

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Starting from *B*,*B*′,*B*′′-triethynylborazine (**1**), an easy construction kit for highly durable Si−B−C−N ceramic materials is presented. Hydrosilylation of **1** with $HSiRCl_2$ (R = Cl, Me, Ph) using Pt/C as catalyst results in the novel precursor molecules **2** and **3**. Subsequent linking reactions with $MeNH_2$ or hydrogenation with $LiAlH_4$ leads to the preceramic precursors **4**−**6**. All compounds and polymers have been characterized by NMR and IR spectroscopy and mass spectrometry. The thermal conversion of **4**−**6** results in various Si−B−C−N ceramics, **C8**−**C10**, with tunable Si, C, and N content. Insights into the mechanism of the pyrolysis have been obtained by thermal analysis as well as IR spectroscopy. The chemical composition of the materials is controlled by the reaction pathway as well as by the backbone of the respective precursor molecules.

1. Introduction

The suitability of silicon-based materials such as Si_3N_4 and SiC for high-temperature applications in material science is undisputed and well established.[1,2] In technical processes, sintering additives are necessary to allow their application, and they also limit the thermal stability of the manufactured materials. In context with this problem, the syntheses of amorphous ceramics, so-called “random inorganic networks”, have been investigated intensively in the past couple decades.[3] Especially, the quaternary Si−B−C−N ceramic materials with outstanding physical and chemical properties became of great interest.[4] In this system, a unique combination of the binary’s properties can be observed. A wide range of different precursors for this multinary non-oxidic ceramic have been tested to date.[5−8]

An important topic in this field of research is the achievement of methods allowing a homogeneous distribution of the constituting elements on an atomic scale. Furthermore, the decomposition of the desired multinary ceramics into their binary phases must be prevented up to high temperatures.[9] This aim may be reached by choosing suitable precursor molecules or preceramic polymers. Typical for all precursor-derived amorphous Si−B−C−N ceramics is a significant amount of silicon and boron with additional nitrogen and carbon contents. The chemical composition of the material can be varied over a certain range using different precursor polymers, molecules, and linking agents in the polymerization step.[5,6,10]

Borazine precursors for Si−B−C−N ceramics have been used several times. Besides our own investigations with silyl-substituted vinylborazines,[11,12] silylmethylborazines[13] and other derivatives[14] have been used as molecular precursors. In another approach, borazines have been attached to poly(vinylsilazanes) via hydroboration or have been used as molecular as well as polymerized precursors for binary and ternary (Si)BCN ceramics.[15]

In this work we present our new findings from experiments directed toward an easy way to control the chemical composition of Si−B−C−N ceramics starting from hydrosilylated *B*,*B*′,*B*′′-triethynylborazine (**1**). In this approach, different chlorosilyl functionalities are introduced in the first step which are either subsequently further modified to give molecular precursors for ceramics (molecule-to-ceramic, MTC, approach) or reacted with primary amines whereby

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preceramic polymers are obtained (polymer-to-ceramic, PTC, approach).

As will be shown, the thermal behavior as well as the thermal conversion process is dominated by the extremely stable vinylborazine backbone of the precursors.

2. Experimental Section

2.1. General Comments. All syntheses were performed in carefully dried glassware under an argon atmosphere, which was passed through the Oxisorb gas purification system of Messer-Griesheim to remove the last traces of oxygen and moisture. All solvents were dried and purified using standard procedures and were freshly distilled under argon from sodium/benzophenone (THF, benzene, *n*Bu$_3$N) or LiAlH$_4$ (hexane, toluene) prior to use. Air-sensitive compounds were stored and weighed in a glovebox (Braun MB 150 B-G system), and reactions on a small scale were performed directly in the glovebox. Bulk pyrolyses of the precursors were performed in quartz tubes up to 1000 °C and in alumina tubes up to 1600 °C under a steady stream of argon. The samples were heated in carbon crucibles at a heating rate of 5 K/min and with a dwell time of 10 h at maximum temperature. Solid samples were pulverized in a WC ball mill in a glovebox.

NMR spectra were taken on a Bruker Avance 400 and Avance 300 system, respectively. The chemical shifts are reported on the δ scale in parts per million relative to the residual nondeuterated solvent signal (^{1}H) or the signal of the deuterated solvent (^{13}C) as an internal standard or relative to the tetramethylsilane signal (^{29}Si) or BF$_3$·OEt$_2$ signal (^{11}B) as an external standard. ^{29}Si chemical shifts of the solid samples were determined relative to the signal of the external standard Q$_8$M$_8$. Values where than expressed relative to the signal of the reference compound TMS (0 ppm). ^{11}B MAS NMR spectra were determined relative to that of an aqueous solution of boric acid, which has a chemical shift of 19.6 ppm relative to the signal of the ^{11}B reference compound BF$_3$·OEt$_2$ (0 ppm). Coupling constants, *J*, are given in hertz and as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, and t for singlets, doublets, and triplets, respectively. Broadened resonances are indicated as br. Mass spectra were taken on a Finnigan MAT SSQ 7000 in the EI (70 eV) mode. IR spectra were recorded with a Perkin-Elmer Spectrum 2000 NIR−FT-Raman spectrometer. Energy values are given in cm^{-1}. Thermal analyses were taken on a NETZSCH STA 409 under a dynamic Ar atmosphere with a heating rate of 10 K/min in corundum crucibles ($T_{\max} = 1500$ °C) or C crucibles ($T_{\max} = 2000$ °C, He). For scanning electron microscopy (SEM), performed on a LEO 1530 (FEG) microscope with 1 kV electrons, samples were fixed on carbon pads. C/N analyses were performed on a LECO CHN-900 analyzer. For X-ray powder investigations a STOE STADI P2 diffractometer (Ge monochromator, Cu Kα_1 = 154.056 pm) was used. Samples have been measured in glass capillaries 0.3 mm in diameter.

2.2. Synthesis. The synthesis of *B,B′,B″*-tris(trichlorosilylvinyl)-borazine (**2c**) as well as **P5c** and **4c** is reported in ref 11. For all experiments described in this paper, the nearly isomerically pure C$_\beta$-substituted product of the monosilyl compounds was used.

B,B′,B″-Tris(dichlorophenylsilylvinyl)borazine, *B$_3$N$_3$H$_3$(CH═CHSiPhCl$_2$)$_3$* ***(2a)***. In a 100 mL Schlenk flask with a magnetic stirrer, 160 mg of Pt/C (1 wt %, 0.008 mmol of Pt) and 1 g (6.5 mmol) of **1** were dissolved in 60 mL of toluene, and afterward, 3.6 g of HSiPhCl$_2$ (3 mL, 0.02 mol) was added. After the solution was heated at 105 °C for 24 h, the Pt/C catalyst was removed by filtration, and residual HSiPhCl$_2$ and toluene were removed under vacuum. The colorless oil was dried under vacuum (<0.1 mbar) at 50 °C for several hours to give the crude product as a mixture of isomers in 95% (4 g) yield. NMR (C$_6$D$_6$): (^{1}H) 4.95 (br, 1H, NH), 6.59 (d, 1H, C*H*═CHSi, $^{3}J_{\mathrm{H,H}}$ = 21.3 Hz), 6.93 (d, 1H, CH═C*H*Si, $^{3}J_{\mathrm{H,H}}$ = 21.3 Hz), 7.8 (br, 5H, Ph); (^{11}B) 34.0; (^{13}C) 140.5 (CH═*C*HSi), 151.4 (*C*H═CHSi), 128.4$^{(p)}$/131.8$^{(m)}$/133.9$^{(o)}$/133.9$^{(i)}$ (Ph); (^{29}Si) 3.7. IR (cm^{-1}): 3411 (N−H); 1592 (C═C); 1459, 1346 (B−N, Ph); 999 (C═C−H). MS: *m*/*z* (rel intens, ion) = 683 (3, M), 648 (3, M − Cl), 606 (5, M − Ph), 508 (19, M − SiCl$_2$Ph), 175 (100, SiCl$_2$Ph).

B,B′,B″-Tris(dichloromethylsilylvinyl)borazine, *B$_3$N$_3$H$_3$(CH═CHSiMeCl$_2$)$_3$* ***(2b)***. Reagents and conditions: 500 mg of **1** (3.3 mmol); 75 mg of Pt/C (1 wt %, 0.004 mmol of Pt); 1.2 g of HSiMeCl$_2$ (1.1 mL, 10 mmol); 80 °C; Yield: 91% (1.5 g). NMR (C$_6$D$_6$): (^{1}H) 0.7 (s, 3H, CH$_3$), 4.86 (br, 1H, NH), 6.44 (d, 1H, C*H*═CHSi, $^{3}J_{\mathrm{H,H}}$ = 21.3 Hz), 6.80 (d, 1H, CH═C*H*Si, $^{3}J_{\mathrm{H,H}}$ = 21.3 Hz); (^{11}B) 35.4; (^{13}C) 4.5 (CH$_3$), 139.2 (CH═*C*HSi), 153.3 (*C*H═CHSi); (^{29}Si) 16.5. IR (cm^{-1}): 3429 (N−H); 1589 (C═C); 1464, 1350 (B−N); 1006 (C═C−H); 2966/1261/786 (CH$_3$). MS: *m*/*z* (rel intens, ion) = 497 (2, M), 384 (11, M − SiCl$_2$Me), 357 (3, M − CH═CHSiCl$_2$Me).

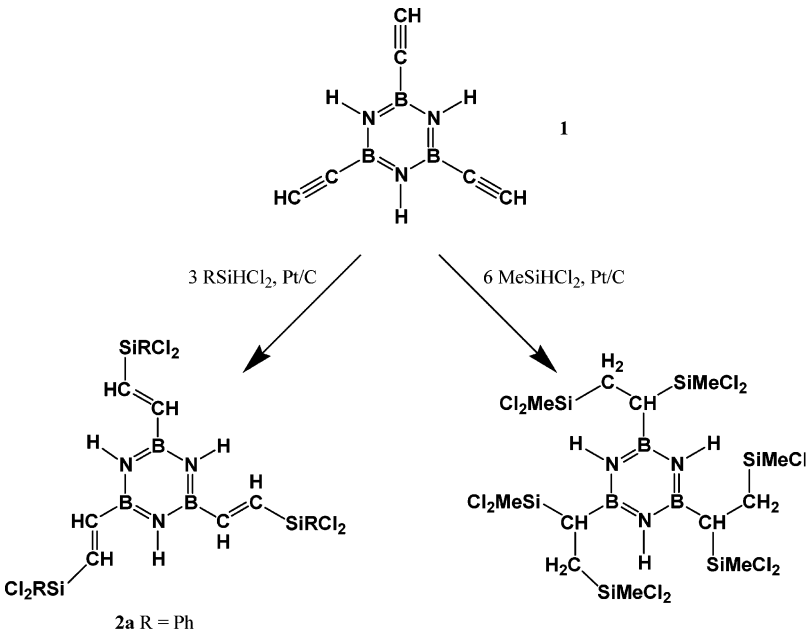
B,B′,B″-Tris[1,2-bis(dichloromethylsilyl)ethyl]borazine, *B$_3$N$_3$H$_3$[CH(SiMeCl$_2$)CH$_2$(SiMeCl$_2$)]$_3$* ***(3)***. In a 100 mL Schlenk flask with a magnetic stirrer, 80 mg of Pt/C (1 wt %, 0.004 mmol of Pt) and 500 mg (3.3 mmol) of **1** were dissolved in 80 mL of toluene, and afterward, 4.9 g of HSiMeCl$_2$ (4.5 mL, 0.01 mol) was added. After the solution was refuxed for 24 h, the Pt/C catalyst was removed by filltration, and residual HSiMeCl$_2$ and toluene were removed under vacuum. The colorless oil was dried under vacuum (<0.1 mbar) for several hours to give the crude product in 90% (2.5 g) yield. Colorless crystals can be obtained by crystallization from hexane at −25 °C. NMR (C$_6$D$_6$): (^{1}H) 0.65 (s, 3H, Si$^{\alpha}$CH$_3$), 0.68 (s, 3H, Si$^{\beta}$CH$_3$), 1.22 (m, 2H, C*H*$_2$CH$_2$Si), 1,24 (m, 2H, CH$_2$C*H*$_2$Si), 5.0 (br, 1H, NH); (^{11}B) 35.0; (^{13}C) 4.7 (Si$^{\beta}$CH$_3$), 5.3 (Si$^{\alpha}$CH$_3$), 17.0 (CH*C*HSi), 18.6 (*C*HCHSi); (^{29}Si) 31.7 (Si$^{\beta}$), 32.0 (Si$^{\alpha}$). IR (cm^{-1}): 3429 (N−H); 1456, 1401, 1354 (B−N); 1091 (C−C−H); 2961/1260/781 (CH$_3$). MS: *m*/*z* (rel intens, ion) = 842 (2, M), 788 (2), 729 (3, −Si(Cl)$_2$Me), 587 (12, −C(H(SiCl$_2$Me))CH$_2$Si(Cl)$_2$Me), 220 (100, •C(H(SiCl$_2$Me))CH$_2$SiCl$_2$Me).

B,B′,B″-Tris[(dihydrophenylsilyl)vinyl]borazine, *B$_3$N$_3$H$_3$(CH═CHSiPhH$_2$)$_3$* ***(4a)***. In a 50 mL Schlenk flask equipped with a 10 mL dropping funnel and a magnetic stirrer, 167 mg (4.5 mmol) of LiAlH$_4$ was suspended in 20 mL of THF, and the suspension was cooled to −20 °C. Under vigorous stirring at −20 °C, 2 g (3 mmol) of **2a**, dissolved in 10 mL of THF, was added over a period of 10 min. The reaction mixture was slowly allowed to warm to room temperature and stirred for 15 h. After addition of 5 mL of benzene, the suspension was filtered over Celite. Subsequently, the solvents were removed in a vacuum, and the residue was extracted with benzene to isolate the product. After evaporation of the benzene and drying under vacuum (10^{-2} mbar), 0.84 g (1.5 mmol, 50%) of **4a** was obtained as a white solid.

NMR (C$_6$D$_6$): (^{1}H) 3.7 (d, 2H, SiH), 4.9 (s, 1H, NH), 6.6 (br, 2H, C*H*═C*H*), 7.65 (m, 5H, Ph); (^{11}B) 31.7; (^{13}C) 139.5 (CH═*C*HSi), 153.2 (*C*H═CHSi), 128.5/131.9/134.1 (Ph); (^{29}Si) −36.6 ($^{1}J_{\mathrm{Si,H}}$ = 197 Hz). IR (cm^{-1}): 3428 (N−H); 2138 (Si−H$_{\mathrm{strech}}$); 1589 (C═C); 1464, 1347 (B−N/Ph); 1008 (C═C−H); 933 (Si−H$_{\mathrm{bend}}$). MS: *m*/*z* (rel intens, ion) = 477 (22, M), 376 (100, M − PhSiH$_2$). DTA/TG: 54.4% weight loss.

[N$_3$B$_3$H$_3${CH═CHSiPh(NMe)$_{1-x/2}$(NHMe)$_x$}$_3$]$_n$ ***(P5a)***. In a 100 mL Schlenk flask equipped with a coolable 50 mL dropping funnel and a magnetic stirrer, 3 g (4.4 mmol) of **2a** was dissolved in 50 mL of hexane, and the solution was cooled to approximately −30 °C. Under vigorous stirring, 4 mL (85 mmol) of methylamine at −30 °C was added over a period of ∼30 min. During the exothermic reaction, the temperature was controlled not to rise

Scheme 1. Hydrosilylation Reactions of *B,B′,B″*-Triethynylborazine Using Pt/C (1% Weight)[a]



1

2a R = Ph
2b R = Me
2c R = Cl

3

[a] For $HSiCl_3$ only a single hydrosilylation takes place

above −30 °C. After being warmed to room temperature, the mixture was stirred for 2 d. The solution was separated by filtration, and the residue was carefully washed with 3 × 30 mL of hexane. Finally, all volatile components were removed in a vacuum (10^{-2} mbar) to produce 13.3 g of **P5a** as a slightly yellow and highly viscous liquid that is very sensitive to moisture and air. NMR (C_6D_6): (^{1}H) 0.74 (SiNH), 2.67 (NCH_3), 5.3 (NH), 6.8 (C*H*=C*H*Si), 7.6 (Ph); (^{11}B) 32.0 (br); (^{13}C) 27.6 (N*C*H_3), 145.0 (CH=*C*HSi), 149.1 (*C*H=CHSi), 128−135 (Ph); (^{29}Si) −25.1. IR (cm^{-1}): 3418 (N−H); 1587 (C=C); 1463, 1370 (B−N, Ph); 1013 (C=C−H), 2888, 2808, 820 (N−*C*H_3). DTA/TG: 29.1% weight loss.

$[N_3B_3H_3\{CH{=}CHSiMe(NMe)_{1-x/2}(NHMe)_x\}_3]_n$ (***P5b***). Reagents: 1 g (2 mmol) of **2b** in 40 mL of hexane; 3.5 mL (75 mmol) of methylamine. Yield: 0.85 g. NMR (C_6D_6): (^{1}H) 0.27 ($SiCH_3$), 0.45 (SiNH), 2.60 (NCH_3), 5.4 (NH), 6.8 (C*H*=C*H*Si); (^{11}B) 33.5 (br); (^{13}C) −3.2 ($SiCH_3$), 27.5 (N*C*H_3), 147.0 (CH=*C*HSi), 147.6 (*C*H=CHSi); (^{29}Si) −16.9. IR (cm^{-1}): 3415 (N−H); 1591 (C=C); 1465, 1370 (B−N); 1011 (C=C−H), 2888, 2808, 1253, 820, 789 (Si−*C*H_3, N−*C*H_3). DTA/TG: 38.8% weight loss.

$[N_3B_3H_3\{\{CH[SiMe(NMe)_{1-x/2}(NHMe)_x]\}\{CH_2[SiMe(NMe)_{1-x/2}(NHMe)_x]\}\}_3]_n$ (***P6***). Reagents: 500 mg (0.58 mmol) of **2b** in 30 mL of hexane; 0.5 mL (11 mmol) of methylamine. Yield: 350 mg. NMR (C_6D_6): (^{1}H) 0.23 ($SiCH_3$), 0.45 (SiNH), 0.8−1.2 (CH_2-CH_2), 2.60 (NCH_3), 5.3 (NH); (^{11}B) 32.5 (br); (^{13}C) −3.6 ($SiCH_3$), 9.6−10.0 (*C*H_2*C*H_2), 26.6 (NCH_3); (^{29}Si) −1.9. IR (cm^{-1}): 3421 (N−H); 1458, 1426, 1367 (B−N); 1103 (C−C−H); 2883, 2803, 1251, 802 (Si−*C*H_3, N−*C*H_3). DTA/TG: 34.4% weight loss.

$[N_3B_3H_3\{CH{=}CHSi(N{=}C{=}N)_{1.5}\}_3]_n$ (***P7***). In a 100 mL Schlenk flask, 250 mg (0.45 mmol) of **2c** and 750 mg (4 mmol) of *n*Bu_3N were dissolved in 50 mL of THF, and the solution was cooled at −78 °C. An 85 mg (2 mmol) sample of H_2N_2C in 10 mL of THF was added dropwise over a period of 15 min under vigorous stirring. The reaction mixture was warmed to room temperature and stirred for 48 h, whereby a white solid separated. After filtration the crude product was extracted with THF for 12 h to remove residual *n*$Bu_3N \cdot HCl$. Finally, the slightly yellow solid was dried under vacuum (<10^{-2} mbar) at 100 °C to give a 95% (166 mg) yield of **P7**. ^{29}Si MAS NMR: −70. IR (cm^{-1}): 3421 (N−H), 2122 (N=C=N), 1582 (C=C); 1456, 1344 (B−N); 1065 (C=C−H); 747 (Si−N). DTA/TG: 42.0% weight loss.

3. Results and Discussion

3.1. Synthesis. As reported previously, the synthesis of silyl-substituted vinylborazines can be performed in quantitative yields using Pt on charcoal as catalyst.[11] Hydrosilylations of *B,B′,B″*-triethynylborazine (**1**) with an excess of silanes $HSiRCl_2$ (R = Cl, Me, Ph) gave different results (Scheme 1). Equimolar reactions yield the desired silylvinyl-substituted products **2a**−**c** with a high regioselectivity (>80% of the *β*-substituted isomer). Remarkably, a double hydrosilylation to bis(silyl)alkyl-substituted compounds was observed with $HSiMeCl_2$, which gave the new compound *B,B′,B″*-tris[1,2-bis(dichloromethylsilyl)ethyl]borazine (**3**). To our knowledge, the Pt/C catalyst has been successfully used for monohydrosilylations of C≡C bonds while double hydrosilylations were not achieved.[16,17] That only monohydrosilylation is observed with $HSiCl_3$ probably has electronic reasons,[18] and is sterical in origin in reactions with $HSiPhCl_2$. For all further manipulations we used the crude reaction mixtures containing both the α- and *β*-substituted isomers.

Subsequent hydrogenations of **2a**,**c** have been performed with $LiAlH_4$ in THF as discussed in a previous paper in detail.[11] The fabrication of the preceramic polymers was performed with **2a**−**c** and **3** and $MeNH_2$ as cross-linking agent, which was employed in large excess.

3.2. Precursor Characterization. Both the monomer and the polymer precursors **2**−**6** have been characterized by

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Table 1. Selected NMR Shifts for 2a−c and 3 in C_6D_6 (δ, ppm)[a]

substitutent at borazine ring	$\delta(^1H)$ of $BC_\alpha H/C_\beta H$	$\delta(^{11}B)$	$\delta(^{13}C)$ of BC_α/C_β	$\delta(^{29}Si)$ of $BC_\alpha Si/C_\beta Si$
[CH═CH(SiPhCl$_2$)] (**2a**)	6.59/6.93	34.0	140.5/151.4	−/3.7
[CH═CH(SiMeCl$_2$)] (**2b**)	6.44/6.80	35.4	139.2/153.3	−/16.5
[CH═CH(SiCl$_3$)] (**2c**)[11]	6.22/6.85	34.0	137.4/153.6 (br)	−/−3.3
[CH(SiMeCl$_2$)CH$_2$(SiMeCl$_2$)] (**3**)	1.24/1.22	35.0	18.6/17.0	32.0/31.7

[a] Further NMR data are given in the Experimental Section. α/β position relative to the borazine ring.

Table 2. Selected NMR Shifts for the Preceramic Precursors 4a−c, P5a−c, and P6 in C_6D_6 (δ, ppm)[a]

	$\delta(^1H)$ of $BC_\alpha H/C_\beta H$	$\delta(^{11}B)$	$\delta(^{13}C)$ of BC_α/C_β	$\delta(^{29}Si)$ of $BC_\alpha Si/C_\beta Si$
[CH═CH(SiPhH$_2$)] (**4a**)	6.7/6.5	31.7	139.5/153.2	−/−36.6
[CH═CH(SiH$_3$)] (**4c**)[11]	6.8/6.4	33.4	135.5/153.7 (br)	−/−62.9
P5a	7.4/7.8	32 (br)	145.0/149.1	−/−25.1
P5b	6.8 (br)[b]	33.5 (br)	147.6/147.0	−/−16.9
P5c[11]	6.8 (br)[b]	35.3 (br)	145.2/147.5 (br)	−/−35.8
P6	1.0 (br)	34.0 (br)	9.8 (br)	1.1/−1.9

[a] Further NMR data are given in the Experimental Section. α/β position relative to the borazine ring. [b] Signal width ~60 Hz, includes both β and α protons.

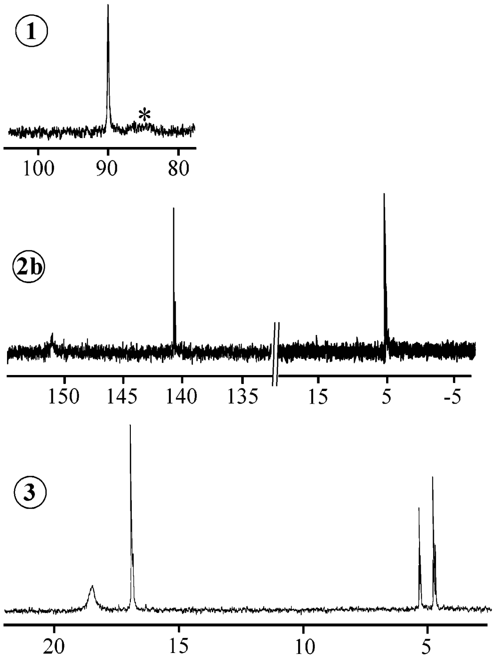

Figure 1. ^{13}C NMR spectra (C_6D_6) demonstrate the change of the shift values of the B−C−C bonds in **1**, **2b**, and **3**. At ~5 ppm, $SiCH_3$ substituents of **2b** and **3** are found. The asterisk indicates the signal of the α-C in **1** with very low intensity due to the quadrupole moment of the boron nucleus (T_1 = 60 s, $w_{1/2} \approx 300$ Hz).[19,21]

NMR and IR spectroscopy and mass spectrometry. Isotropic ^{11}B NMR shifts of all compounds are in the typical range of 29−32 ppm and are more broadened for the polymers **P5a−c** and **6**.[19] For monitoring the chemical reactions, ^{13}C NMR shifts were used which were found to be characteristic for each type of compound (Figure 1). While a resonance at 91 ppm is characteristic for the C≡*C*H in **1**, the ^{13}C resonances of the β-hydrosilylated main products **2a−c** are observed at ~140 ppm (C_β) and ~150 ppm (C_α, weak and broadened[19]) (see Table 1). In the doubly hydrosilylated compound **3**, the ^{13}C shift of the boron-bonded carbon of the alkyl group is drastically shifted to lower frequencies of 17.0 ppm (C_β) and 18.6 ppm (C_α, broad). Methyl groups at silicon of **2b** and **3** show their resonances at ~5 ppm. The phenyl substituents at silicon show three signals at 128.4, 131.8, and 133.9 ppm in **2a** (similar to values for **4a** and **5a**; see the Experimental Section). The *ipso*-carbon of the Ph group in **2a** was detected by an HNMBC[20] experiment and found at the same position as the *o*-C at 133.9 ppm. In accordance with carbon NMR, ^1H shifts show similar effects (see the Experimental Section). The resonances of the protons attached to the α-carbon (with respect to the borazine ring) in **2a−c** and **4a−c** are observed at ~6.5 ppm, while the protons at C_β show their resonances around 6.9 ppm. The stereochemistry at the C═C bond in **2a**,**b** is indicated by a $^3J_{H,H}$ coupling constant of 21.3 Hz, similar to that of the trichloro derivative **2c** (21.8 Hz), which was characterized by a single-crystal X-ray analysis.[21] In the disilyl derivative **3**, ^1H NMR shifts of the $SiCH_3$ substituents are seen at 0.65 ppm (α) and 0.68 ppm (β) and alkyl protons at 1.24 ppm (BC*H*) and 1.26 ppm (BCC*H*). The assignments are also based on an HNMBC experiment.[20]

The characteristic ^{29}Si NMR shifts are in nearly perfect agreement with literature data and the established increment system.[17,22] An exchange of the chlorine substituents C═CSiRCl$_2$ in **2a−c** to C═CSiRN$_2$ (N = amino group) in the polymers **P5a−c** is accompanied by a low-frequency shift by ~30 ppm (see Tables 1 and 2). Subsequent hydrogenation of **2a**,**c** leads to a further low-frequency shift of the ^{29}Si resonances: −36.6 ppm for C═CSiPhH$_2$ in **4a** as well as −62.9 ppm for C═CSiH$_3$ in **4c**.[11]

Further useful fingerprints indicative of the structures of the precursor compounds are provided by IR spectroscopy. In all precursors **2**, **4**, and **5** the C═C stretching mode at ~1590 cm^{-1} and the corresponding C═C−*H* bending vibration at ~1010 cm^{-1} are recorded. In contrast, the C−C stretching mode of the doubly hydrosilylated initial C≡C bond in **3** and **P6** is observed at ~1100 cm^{-1}. Most importantly, the characteristic N−B−N vibration modes of the B_3N_3 ring are observed in all precursors **2−6** at about 1470, 1340, and 800 cm^{-1}.[21,23] In **2a**, **4a**, and **5a** these modes overlap with the phenyl modes arising from the silyl substituent. Modes of the methyl groups in the methylsilyl-substituted compounds are measured at 2960, 1260, and 780 cm^{-1}. Compared to those of the trihydrosilyl compound **4c**, the typical Si−H modes of **4a** are shifted to higher energies

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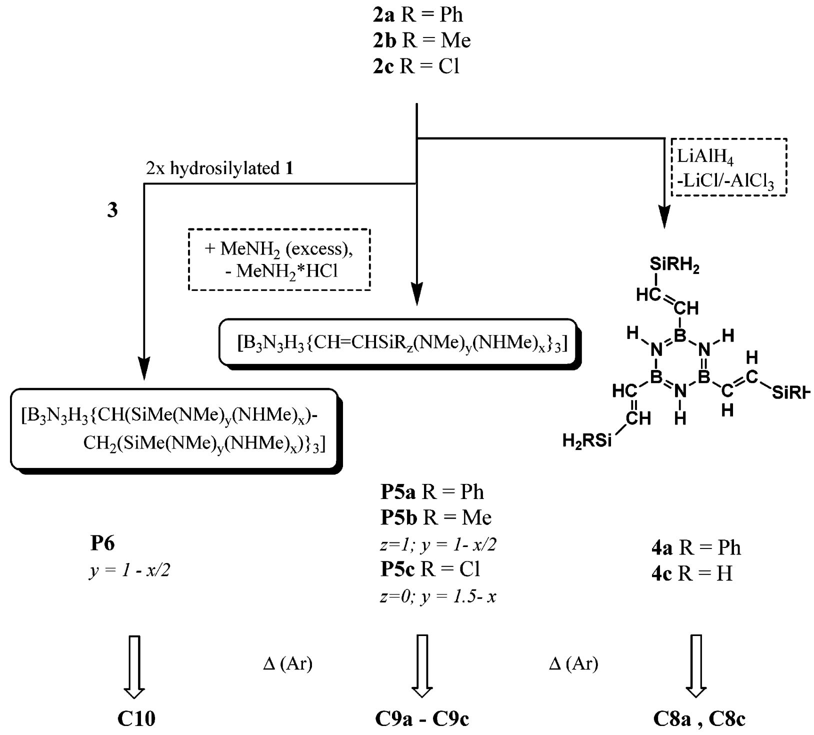
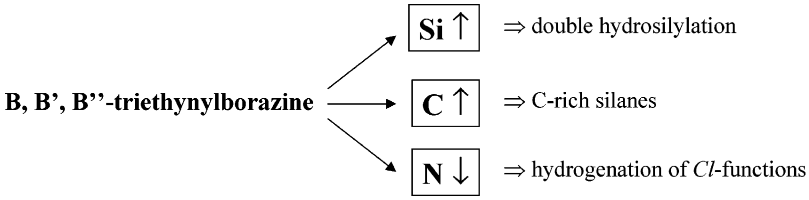
Scheme 2. Syntheses of Different Preceramic Polymers P5 and P6 via Aminolysis of 2 and 3, Respectively, as Well as Hydrogenation Reactions of 2[a]



[a] Both polymer and monomer precursors are thermally converted to $Si_xBN_yC_z$ ceramics **C8**−**C10**.

Scheme 3. Construction Kit for the Chemical Composition of Si−B−C−N Ceramics Starting from 1



for the bending mode (at ~940 cm^{-1}) and to lower energies for the stretching mode (at ~2130 cm^{-1}).

The reaction of **2c** with cyanamide results in the extremely air-sensitive carbodiimide precursor **P7**, which forms a solid comparable to an oxygen-bridged silylvinylborazine-based silica gel[21] and other solid polymer precursors.[6,24] All functional groups could be detected by IR spectroscopy. The ^{29}Si NMR shift at −70 ppm is typical for a C=CSi(N=C=N)$_3$ unit.[25] Compared to those of the polymers **P5a**−**c** and **6**, the vinyl (1582 cm^{-1}) and borazine (1456/1344 cm^{-1}) modes are slightly broadened but have similar vibration energies. An additional strong mode at 2122 cm^{-1} is clearly assigned to the N=C=N vibration.

3.3. Ceramic Material Characterization. The thermal conversion of the polymeric precursors **P5a**−**c** and **P6** and molecular precursors **4a**−**c** to the desired ceramics (**C8a**,**c**, **C9a**−**c**, and **C10**, respectively) has been carried out in carbon crucibles (Sigradur) under a dynamic argon atmosphere. Applying a heating rate of 5 K/h, the samples were pyrolyzed in a first step up to 1000 °C in quartz tubes, and then up to 1600 °C in alumina tubes. After this thermal treatment, both polymeric or molecular precursors gave black and dense amorphous ceramic materials (Scheme 2, Figure 5a). The conversion process was monitored by thermal analyses, and the final product was characterized by X-ray powder diffraction, chemical analysis, MAS NMR spectroscopy, and electron microscopy (SEM and transmission electron microscopy (TEM); see Figure 5b,d).

Taking advantage of the characteristic vibration modes discussed above, we investigated the thermal conversion processes by IR spectroscopy in some detail. As described in the literature, major thermal rearrangements can be observed in the temperature range up to 600 °C.[26] As shown in Figure 2, the IR modes of the silazane methyl groups in the range of 2800−2960 cm^{-1} are removed completely at 200 °C. Above 200 °C, the vinyl modes are first shifted to higher energies. Further heating to 600 °C leads to a broadening of this vibration mode concomitantly with a reshift to energies of about 1600 cm^{-1}. During this whole process, the borazine ring modes are continuously broadened but remain observable in the observed temperature range.

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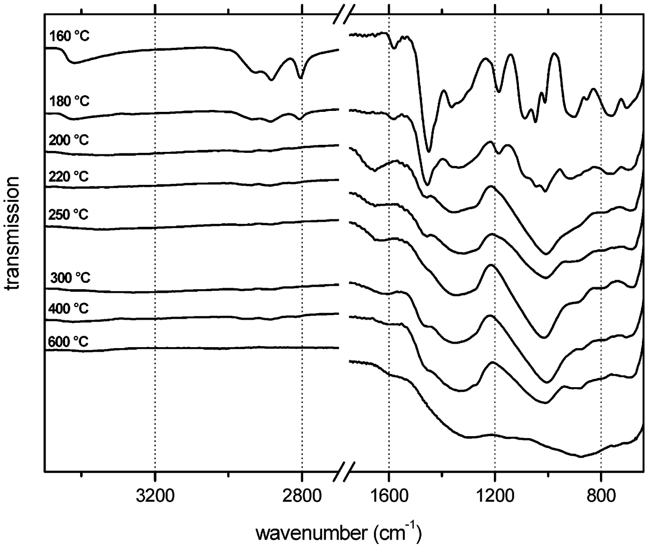

Figure 2. IR spectra of **P5c** after being annealed at different temperatures. The polymer was crushed after a first heating at 150 °C, and each sample was held at the mentioned temperature for 3 d.

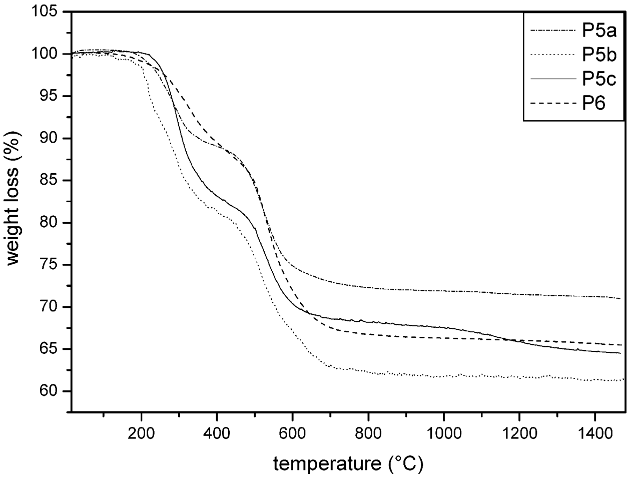

Figure 3. TG diagrams of the polymeric precursors **P5a−c** and **P6** (heating rate 10 K/min, flowing argon).

Also, the Si−N vibration modes can be observed at each temperature and finally become the second dominant modes at elevated temperatures.

The weight loss and amount of gaseous byproducts during pyrolysis are of special interest for the ceramic formation. As reported previously, TG measurements with **P5c** up to 1500 °C showed a total weight loss of approximately 37%.[11] The polymeric precursors **P5a**,**b**, and **P6** show a very similar thermal conversion behavior in this temperature range (Figure 3). The thermal process detected in the first step (250−450 °C) is assigned to the completion of the polycondensation reaction. In the second step in the range of 450−650 °C, fragmentations in the prepolymer lead to a further weight loss. According to TG−MS investigations,[11] a loss of the silicon-bonded hydrocarbon substituents (methyl, phenyl) prevails in this temperature range, which causes a weight loss of ~14% for **P5c**. A simultaneously recorded DTA (not quantitative) shows two major thermal effects at 500−550 and ~1100 °C for all polymer precursors.[28] The methlysilyl- and phenylsilyl-substituted precursors **P5a,b** and **P6**, respectively, show an additional DTA effect at ~900 °C, and a lower peak intensity is observed at ~1100 °C. As expected, the overall weight loss of the phenyl-substituted polymer **P5a** (70.9% ceramic yield) is the lowest one due to a particular incorporation of the phenyl group into the ceramic material. The lowest ceramic yield (61.2%) was observed with the $SiMeCl_2$-monosubstituted polymer **P5b**, which is presumably due to the preferred formation of methane. In the thermal conversion of the bis(dichloromethylsilyl)-substituted polymer **P6** (ceramic yield 65.6%), about 90% of the silicon content remains in the ceramic material (vide infra).

We previously reported that the pyrolysis of the SiH_3-substituted molecular precursor **4c** gives a nitrogen-poor ceramic in very high yield (94%).[11] In relation to the results obtained with the polymeric ceramic precursors described above, it was of interest to try to prepare a carbon-rich ceramic using the $SiPhH_2$-substituted molecular precursor **4a**. However, corresponding to chemical analysis (vide infra), the weight loss in the pyrolysis of **4a** is higher (low ceramic yields in the range of 55%) likely due to the reaction of the phenyl substituent with liberated hydrogen. Only small amounts of the phenyl carbons are incorporated into the ceramic material.

It has been reported that the linking of mono- and oligosilanes with H_2N_2C leads to precursors for multinary ceramics in high yields.[6,27] We therefore hoped that our solid cyanamide-bridged polymer **P7** would equally give a Si−B−C−N ceramic in high yield (theoretically 97% can be expected). The thermal behavior of **P7** was tested by a standard DTA/TG measurement ($T_{max} = 1200$ °C). Disappointingly, a weight loss of 42% and a main thermal effect are observed between 600 and 900 °C employing a heating rate of 10 K/min. A lower heating rate (5 K/h) in the standard pyrolysis procedure (see the Experimental Section) results in a higher ceramic yield of **C11** (~70%). This behavior is in contrast to that of the previously described liquid polymers **P5a−c**, which give independently of the heating rate the same ceramic yield (within the experimental errors). The obtained ceramic **C11** is a fine powder in contrast to the ceramics **C8−C10**, which are obtained as dense bulk materials.

X-ray powder investigations of all ceramics demonstrate the amorphous character of the material up to 1500 °C. For the carbon-rich phase **C9a**, a very weak and broad reflection at $2\theta \approx 43°$ can be observed according to the formation of layered *h*-BN or graphite. HRTEM investigations reveal the completely amorphous state on the atomic scale of the samples heated to 1600 °C except small domains of graphite/*h*-BN layers for **C9a**. SEM images show a dense surface of the obtained ceramic particles without any visible pores (see Figure 5). High-temperature (HT) thermal analysis of **C8c**, **C9c**, and **C10** shows weight losses of maximum 1−2% up to 2000 °C; that is, no decomposition of the material is observed. However, rearrangement into crystalline phases

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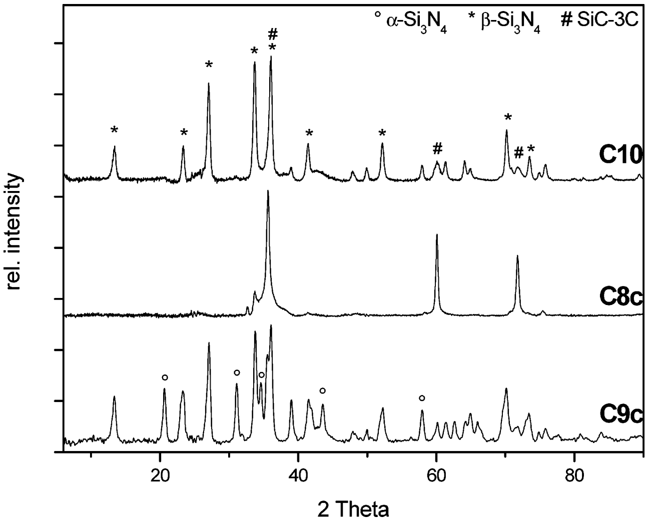

Figure 4. X-ray powder pattern of the ceramic materials **C8c**, **C9c**, and **C10** after HT thermal analysis up to 2000 °C.

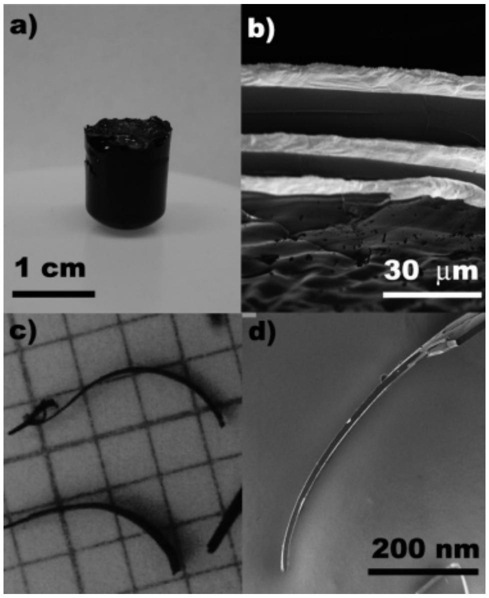

Figure 5. As-obtained ceramic materials: (a) bulk material after pyrolysis in the carbon crucible; (b) a composite made of alumina foil (bright area) on a film of the prepolymer **P5c** was deposited and pyrolyzed at 600 °C; (c, d) thin isolated layers of the ceramic **C9c** prepared from **P5c** at 1000 °C.

embedded in an amorphous B−C−N matrix is observed which depends on the chemical composition of the initial ceramic material.[29] The nitrogen-poor phase **C8c** forms exclusively SiC−3C, while **C9c** and **C10** form SiC−3C as well as Si_3N_4 (Figure 4). The stability of Si_3N_4 up to these temperatures causes, first, a high internal N pressure and, second, a diffusion barrier due to the adjacent B−C−N matrix. Thermoanalytical investigations up to 1200 °C in air show no significant weight loss. Effects of ∼2% result probably from surface reactions discussed in the literature.[10]

From ^{11}B and ^{29}Si MAS NMR experiments, no significant differences have been observed for all ceramic materials **C8**−**C10**. The results are in accordance with previous reports: For the boron centers (^{11}B, $\delta_{iso} = 30$ ppm) a trigonal planar and for the silicon centers ($\delta \approx -45$ ppm) a tetrahedral coordination sphere is indicated by typical chemical shifts.[11,30]

Table 3. Calculated and Measured Elemental Composition (wt %) of Ceramics C8a,c, C9a−c, and C10 and the Corresponding Formulas[a]

material	Si/B ratio (calcd)	N	C	empirical formula	calcd formula
C8a	0.89 (1.0)	14.3	38.7	$Si_{0.89}BC_{2.7}N_{1.0}$	$SiBC_{2+x}N$
C8c[11]	1.02 (1.0)	14.8	36.8	$Si_1BC_{2.5}N_{0.9}$	$SiBC_2N$
C9a	0.84 (1.0)	17.4	52.3	$Si_{0.84}BC_{5.0}N_{1.4}$	$SiBC_aN_b$
C9b	0.93 (1.0)	25.1	30.8	$Si_{0.92}BC_{2.1}N_{1.5}$	$SiBC_aN_b$
C9c[11]	0.98 (1.0)	35.7	24.1	$Si_1BC_2N_{2.7}$	$SiBC_2N_{2.5}$
C10	1.81 (2.0)	24.5	28.2	$Si_{1.8}BC_{3.1}N_{2.3}$	$Si_2BC_aN_b$

[a] Empirical formulas are standardized at B. Indices *a* and *b* represent values of the molar ratios C/B and N/B, which are variable. Oxygen values are 1−2% and omitted.

For the chemical characterization of the ceramic materials, the Si and B content was determined by laser ablation ICP-MS.[31] As previously described in detail,[11,28] this method allows a very simple handling of the samples and gives precise results. The Si/B ratio was measured for all ceramic materials **C8**−**C10** (Table 3). In contrast to that in the ceramics obtained with **4c** or **P5c**[11], the Si/B ratio in the ceramics prepared from the methyl- and phenyl-substituted precursors **P5a**,**b** and **4a** is slightly decreased. However, it corresponds roughly to the Si/B ratio in the common $B_3N_3(C_2Si)_3$ unit encountered in all precursors. The slightly lower (by 10%) Si content in the ceramics **C8a** and **C9a**,**b** is probably due to the formation of small amounts of volatile silanes during the pyrolysis. The same effect is observed in the pyrolysis of the disilyl-substituted precursor **P6**, where also 10% of the initial silicon content is lost. Nevertheless, a remarkable doubling of the Si content in the ceramic material **C10** is achieved.

The nitrogen content of the ceramic material depends on the synthetic pathway: Hydrogenation leads to a lower N content (B/N ratio ∼1), and polymerization with methylamine increases the N content, depending on the amount of reactive sites of the precursor molecules. That is, for the ceramic **C9c** derived from the trichlorosilyl derivative **2c**, the highest nitrogen content of all synthesized materials is obtained. The carbon content of the ceramics depends, as expected, on the substituent R in **2a**−**c** (see Scheme 2). Especially, phenyl-substituted precursors give high C contents (**C8a** and **C9a** in Table 3). However, when the $SiPhH_2$-substituted precursor **4a** is employed, a rather low carbon content is measured, which may have its origin in the previously mentioned formation of volatile byproducts (e.g., C_6H_6) during pyrolysis.

Conclusions

We demonstrated an easy access to various precursor-derived Si−B−C−N ceramics with a tunable content of C, N, and Si. Our synthetic concept uses, starting from **1**, chlorosilyl-substituted borazines such as **2** and **3** as well-defined common molecular precursors. The silicon functionalities are easily introduced by catalyzed hydrosilylations.

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Compounds such as **2** and **3** can be varied in multiple ways: either by hydrogenation to molecular precursors such as **4a**,**c** or by fabrication of preceramic polymers using various amines as cross-linking agents. The latter approach allows the nitrogen content to be easily controlled in the final ceramic. The differences in the silicon and/or carbon content adjusted in the preceramics (molecular as well as polymeric) is also reflected in the final chemical composition. Mechanistical studies of the pyrolysis process indicate that the vinylborazine backbone is highly stable and most likely incorporated in an intact manner as is mainly indicated by IR spectroscopy and chemical analysis.

Clearly, the 1,2-addition of reactive heteroatom−hydrogen bonds such as H−Si to tris(alkynyl)borazines such as **1** as discussed here can be easily extended to a manifold of others such as H−B, H−Al, H−Sn, and H−M (M = transition metal) and allows a construction kit for functional materials to be set up.

Many possible applications can be foreseen: As shown in Figure 5, layered composite materials (here prepared with aluminum foil; see Figure 5b) and thin ceramic layers (see Figure 5c,d) can be produced. Because carbon-rich ceramics (>50% C) may be promising materials for lithium batteries,[32] we will try to use the concept outlined here for this application. Furthermore, a homogeneous doping or incorporation of different metals (Al, Fe, Ni) into the ceramic materials is under investigation, which hopefully will lead to novel functional materials.[1,8,33]

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