[3] D. Selent, K.-D. Wiese, D. Röttger, A. Börner, *Angew. Chem.* **2000**, *112*, 1694–1696; *Angew. Chem. Int. Ed.* **2000**, *39*, 1639–1641.

[4] E. Billig, A. G. Abatjoglou, D. R. Bryant (UCC Corp.), EP 0214622, **1987** [*Chem. Abstr.* **1987**, *107*, 25126m].

[5] The new compounds were obtained as a mixture of diastereomers and were fully characterized. The experimental details are given in the Supporting Information.

[6] Industrial di-*n*-butene was also used consisting of a mixture of internal and structural isomers of octene. For the individual ligands the selectivities towards conversion into terminal aldehydes are comparable to the values given in Table 1.

A Sol–Gel Route to B_4C[**]

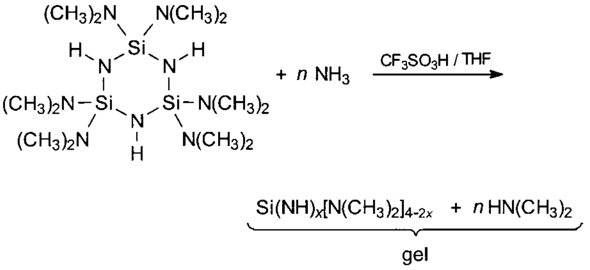
Edwin Kroke,[*] Karl W. Völger,
Alexander Klonczynski, and Ralf Riedel

The classic oxide sol–gel process based on hydrolysis reactions of alkoxides or halides has been examined in detail over several decades.[1] A continuously increasing number of publications indicates that sol–gel processing as a method to produce oxide materials is still gaining importance.[2] In contrast, there have been very few reports on non-oxide sol–gel systems.[3] A sol–gel route to B/(C)/N materials was found in the 1980s by Paine and Narula et al. which is based on "silazanolyses" of *B*-trichloroborazenes with hexa- (HMDS) or heptamethyl disilazane. This sol–gel system was used to prepare B/C/N xerogels, aerogels, and hexagonal boron nitride (h-BN).[4] The crystallization behavior and the oxidation resistance of the products were investigated[5] and molecular model compounds were synthesized and structurally characterized.[6] The results were summarized in a review article and compared with classical routes to boron nitride.[7]

In 1997 it was discovered that chlorosilanes $RSiCl_3$ (with R = H, Cl, alkyl, aryl) form gels in pyridine-catalyzed reactions with bis(trimethylsilyl)carbodiimide.[8] Later, this sol–gel process was extended to dichlorosilanes and functionalized chlorosilanes.[9] Monodisperse spherical particles,[10] Si/C/N coatings and membranes,[11] bulk Si/C/N samples, and pure SiC powder were produced.[12] It is remarkable that this "sol–gel process" is analogous to the oxide system in terms of phenomenological, chemical, physical, and spectroscopic characteristics.[3, 13]

Several attempts to prepare gels from chlorosilanes and HMDS or other silazanes were not successful.[14] Similarly, for carbides or nitrides of elements other than Si, as well as further non-oxide materials such as sulfides, selenides, borides etc., there are very few examples of sol–gel processes known.[3] Most attempts to synthesize non-oxide gels resulted in the formation of solid precipitates.

Recently the first example of a sol–gel process based on ammonolysis has been discovered by Bradley et al., starting from a dialkylamino-substituted cyclic trisilane Si/(C)/N gels were prepared [Eq. (1)].[15]



(1)

B/C/N materials are of interest for several reasons. Novel graphitic ternary phases of these elements may provide materials with properties intermediate between graphite and h-BN.[16] Similarly, sp^3-hybridized B/C/N materials are considered as promising ultra-hard phases combining the properties of diamond and cubic boron nitride (c-BN).[17]

Boron carbide (B_4C) ranks next to diamond in its hardness.[18] It is produced on an industrial scale by classical carbothermal reduction of B_2O_3 in electric arc furnaces. Dense materials are obtained either by pressureless sintering or hot pressing at 2100–2250 °C. B_4C is used for armor plating, blasting nozzles, as mechanical seal faces, and for grinding and cutting tools. The natural presence of the ^{10}B isotope together with chemical inertness and stability under irradiation makes B_4C valuable as a neutron absorber. Because of its ability to generate an electromotive force (EMF) which increases with temperature B_4C has been studied for space power generation and used for high-temperature thermocouples.

In our search for ternary B/C/N phases we examined the reactions of BCl_3 and *B*-trichloroborazene with bis(trimethylsilyl)carbodiimide. It turned out that BCl_3 forms solid, insoluble, and infusible products, which contained either residual chlorine or significant amounts of silicon, depending on the reaction conditions. In contrast, *B*-trichloroborazene ($B_3N_3H_3Cl_3$) reacts with bis(trimethylsilyl)carbodiimide in THF, toluene, or even without any solvent to form non-oxide gels. The xerogels obtained after ageing and drying are practically free of chlorine or oxygen and contain only small amounts of silicon.

The FT-infrared (IR) and Raman spectra clearly indicate the presence of the carbodiimide unit showing the characteristic vibration at 2180 cm^{-1} and 1530 cm^{-1}, respectively.[19] In addition the typical bands for N–H and B–N bonds were observed. Only very weak C–H and Si–CH_3 vibration bands at 2980 cm^{-1} and 1250 cm^{-1} were observed. This corresponds well with the elemental analysis, given in Table 1, that indicate

---

[*] Dr. E. Kroke, Dipl.-Ing. K. W. Völger, Dipl.-Ing. A. Klonczynski,
Prof. Dr. R. Riedel
Technische Universität Darmstadt
FB 11, FG Disperse Feststoffe
Petersenstrasse 23, 64287 Darmstadt (Germany)
Fax: (+49) 6151-166346
E-mail: kroke@hrzpub.tu-darmstadt.de

[**] We are grateful for the financial support from the Deutsche Forschungsgemeinschaft (DFG, Bonn), Fonds der Chemischen Industrie (FCI, Frankfurt), and Bayer AG (Leverkusen). We thank Dr. Florence Babonneau and Dr. Christel Gervais (Université Paris) for the solid-state NMR investigations.

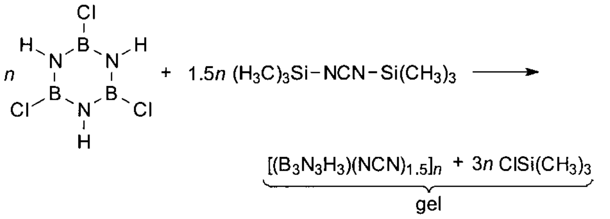
Table 1. Results of elemental analyses [mass %] of the xerogel and the amorphous and crystalline pyrolysis products. The measurements were performed by Analytisches Labor Pascher, Remagen-Bandorf (Germany).

Product	B	C	N	Si	H	O	Cl	Σ	Molecular formula
xerogel (150 °C/10^{-2} Torr/1 h)	19.5	19.1	49.5	5.4	3.8	1.2	0.3	98.8	$BC_{0.88}N_{1.96}Si_{0.11}H_{2.09}O_{0.04}$ (BCN_2H_2)
amorphous product (1200 °C/Ar/2 h)	34.9	8.9	49.7	4.7	< 0.3	1.8	< 0.1	< 100.4	$BC_{0.23}N_{1.1}Si_{0.05}H_{0.09}O_{0.03}$ (B_4CN_4)
crystalline product (2000 °C/He/4 h)	78.3	21.0	n.d.[a]	n.d.[a]	n.d.[a]	n.d.[a]	n.d.[a]	99.3	$BC_{0.24}$ ($B_4C_{0.97}$) (B_4C)

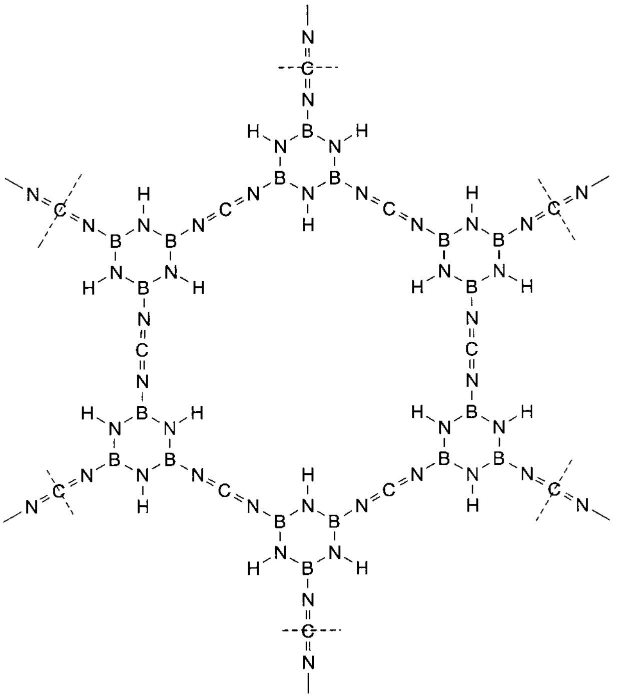
[a] n.d.: not determined.

only minor amounts of $Si(CH_3)_3$ end groups are present in the network.

An idealized reaction is depicted in Equation (2) and a proposed structure of the polymeric network is given in Scheme 1. X-ray diffraction studies confirmed that an amorphous xerogel is present. The solid-state ^{11}B NMR spectrum shows a broad resonance signal centered at $\delta = 15$ which was attributed to boron atoms coordinated by three N atoms, two from the borazene ring and one from a carbodiimide group.



(2)



Scheme 1. Idealized structure of the polymeric carbodiimide borazene network forming the B/C/N gels.

Nitrogen adsoprtion measurements, analyzed according to the Brunauer–Emmett–Teller (BET) model, indicate that the xerogel has a surface area of 85 $m^2 g^{-1}$. This is significantly less than the values of 500–1000 $m^2 g^{-1}$ reported for the Si/N xerogel of Bradley et al. and of many porous oxide xerogels.

The xerogel was pyrolyzed in dry Argon using a heating rate of 100 °C h^{-1}. According to thermogravimetric mass spectrometry (TGA-MS) investigations two major ceramization steps occur. Around 200–300 °C methane is formed causing a mass loss of about 10 %. Larger amounts of nitrogen, as well as methane are formed between 600 and 1000 °C causing another mass loss of about 40 %. This corresponds well with the elemental analysis of the pyrolysis product obtained at 1200 °C (see Table 1). The composition of this amorphous material is close to that of B_4CN_4, which is located on the BN–C and B_4C–N tie-lines in the ternary B/C/N compositional diagram (Figure 1). The carbon content of this substance is relatively low compared to the molecular and polymeric precursor derived B/C/N materials normally investigated. Usually BC_xN phases with $x \geq 2$, for example BC_2N, BC_3N, or BC_4N are prepared and characterized.[16, 17, 20]

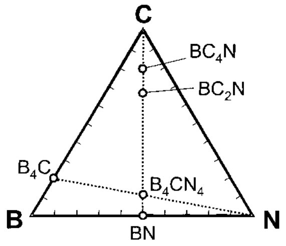


Figure 1. Compositional diagram for the ternary B/C/N system. The amorphous B_4CN_4 produced at 1200 °C is located on the intersection of the C–BN and B_4C–N tie lines.

Annealing the amorphous $B_4CN_4(Si_{0.2})$ at 2000 °C causes the formation of nitrogen and small amounts of volatile silicon-containing species to give pure crystalline B_4C (see Table 1 and Figure 1) as shown by TGA, X-ray diffraction, and elemental analysis. A detailed investigation of the pyrolysis and crystallization process will be published elsewhere.

Here we have reported preliminary results on a carbodiimide-based sol–gel synthesis of B/C/N polymers. These materials are almost free of oxygen, chlorine, and silicon, a remarkable result since often significant amounts of end groups such as, Cl- and $(CH_3)_3Si$- are trapped when three-dimensional networks formed by polycondensation reactions. Pyrolysis of the xerogel at 1200 °C provides an amorphous B_4CN_4 material, which is an interesting precursor for high-pressure/high-temperature experiments to obtain novel graphitic or sp^3 hybridized crystalline B/C/N phases. Furthermore, the xerogel can be transformed into pure B_4C at 2000 °C.

Experimental Section

All manipulations were performed under inert atmosphere using glove box and/or Schlenk techniques. *B*-trichlorborazene[21] and bis(trimethylsilyl)-carbodiimide[22] were synthesized according to the literature methods.

In a typical experiment bis(trimethylsilyl)carbodiimide (1.24 mL) was added to freshly sublimed *B*-trichloroborazene (0.5 g) dissolved in dry toluene (1 mL). The clear solution was heated to 45 °C. After 0.5 h the mixture became cloudy and after 16 h a gel had formed. The product was stored at 45 °C for 30 days. During this ageing period no significant syneresis (contraction) was observed. The gel was dried at 150 °C/10^{-2} Torr. Analogous reactions with a tenfold amount of starting materials were also successful.

In a similar experiment *B*-trichloroborazene (3.9 g) and bis(trimethylsilyl)carbodiimide (9.5 mL) were dissolved in dry THF (50 mL). After 2.5 h reflux the content of the flask suddenly solidified to form a monolithic colorless gel body. The gel was dried at 140 °C/10^{-2} mbar/2.5 h and 190 °C/10^{-2} mbar/0.5 h. Owing to the short ageing period this xerogel contained significant amounts of chlorine (4.75 mass%) and silicon (6.3 mass%).

In other variants *B*-trichlorborazene (0.5–1.5 g) was dissolved in toluene (5–10 mL) or an excess of bis(trimethylsilyl)carbodiimide and stored at 45 °C. The mixtures formed a gel after 1–3 days depending on the concentration. After an ageing period of 2–40 days the gels were dried at 150 °C/10^{-2} Torr.

The xerogels were pyrolyzed in Quartz Schlenk tubes under argon at 400, 600, 800, 1000, and 1200 °C for 2 h using a heating rate of 100 °C$\,h^{-1}$. Further annealing at 1600 and 1800 °C in Ar and at 2000 °C in He was performed in a graphite furnace. Heating rates of 600 °C$\,h^{-1}$ up to 1200 °C followed by 300 °C$\,h^{-1}$ and holding times of 4 h were applied.

The yield of the xerogels, based on the amount of *B*-trichloroborazene and the idealized structure depicted in Scheme 1, was 110–125%, which is because of residual trimethylsilyl end groups. The yield of the B/C/N material obtained at 1200 °C was 58–61% based on the xerogel. Using this amorphous product as a reference the ceramic (boron carbide) yield at 2000 °C is 56%.

The xerogels and pyrolysis products were investigated using FT-IR (Perkin-Elmer FTIR 1750, KBr pellets), Raman (Bruker IFS 55), and ^{11}B NMR spectroscopy (Bruker MSL 400 spectrometer, external standard: $(CH_3CH_2)_2O\cdot BF_3$, 128.28 MHz) as well as nitrogen absorption measurements (Quantachrome Autosorb-3B), elemental analysis (see Table 1), X-ray diffraction (STOE STADI-P-diffractometer, $Cu_{K\alpha}$), and TGA-MS (Netzsch STA 429 coupled with a mass spectrometer Balzers QMG 420).

Received: December 4, 2000 [Z16208]

---

[1] a) C. J. Brinker, G. W. Scherer, *Sol–Gel Science*, Academic Press, San Diego, **1990**; b) *Sol–Gel Science and Technology* (Eds.: M. A. Aergerter, M. Jafelicci, Jr., D. F. Souza, E. D. Zanotto), World Scientific, Singapore, **1989**; c) *Chemistry, Spectroscopy and Applications of Sol–Gel Glasses* (Eds.: R. Reisfeld, C. K. Jorgensen), Springer, Berlin, **1992**; d) *Sol–Gel Technology for Thin Films, Fibers, Preforms, Electronics, and Specialty Shapes* (Ed.: L. C. Klein), Noyes, Park Ridge, **1988**; e) R. Corriu, D. Leclerq, *Angew. Chem.* **1996**, *108*, 1524; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1420.

[2] According to a Chemical Abstracts database search the number of papers related to sol–gel chemistry increased from 1300 in 1993 to about 2600 in 1998.

[3] "Novel Sol–Gel Routes to Non-Oxide Ceramics": E. Kroke, *Proc. 9th CIMTEC World Ceramics Congress, Part C* (Ed.: P. Vincenzini), Techna Srl., Faenza, **1999**, p. 123.

[4] a) C. K. Narula, R. Schaeffer, A. Datye, R. T. Paine, *Inorg. Chem.* **1989**, *28*, 4053; b) R. T. Paine, C. K. Narula, R. Schaeffer, A. Datye, *Chem. Mater.* **1989**, *1*, 486; c) T. T. Borek, X. Qui, L. M. Rayfuse, A. Datye, R. T. Paine, L. F. Allard, *J. Am. Ceram. Soc.* **1991**, *74*, 2587; d) D. A. Lindquist, T. T. Borek, S. J. Kramer, C. K. Narula, G. Johnston, R. Schaeffer, D. M. Smith, R. T. Paine, *J. Am. Ceram. Soc.* **1990**, *73*, 757.

[5] C. K. Narula, R. Schaeffer, A. Datye, T. T. Borek, B. M. Rapko, R. T. Paine, *Chem. Mater.* **1990**, *2*, 384.

[6] C. K. Narula, D. A. Lindquist, M.-M. Fan, T. T. Borek, E. N. Duesler, A. K. Datye, R. Schaeffer, R. T. Paine, *Chem. Mater.* **1990**, *2*, 377.

[7] R. T. Paine, C. K. Narula, *Chem. Rev.* **1990**, *90*, 73.

[8] a) A. O. Gabriel, R. Riedel, *Angew. Chem.* **1997**, *109*, 371; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 384; b) A. O. Gabriel, R. Riedel, S. Storck, W. F. Maier, *Appl. Organomet. Chem.* **1997**, *11*, 833.

[9] a) E. Kroke, A. O. Gabriel, D. S. Kim, R. Riedel, *Organosilicon Chemistry IV* (Eds.: N. Auner, J. Weis), Wiley-VCH, Weinheim, **2000**, p. 812; b) K. W. Völger, Diploma Thesis, Darmstadt University of Technology, **1998**.

[10] Y.-L. Li, E. Kroke, A. Klonczynski, R. Riedel, *Adv. Mater.* **2000**, *12*, 956.

[11] a) A. O. Gabriel, PhD Thesis, Darmstadt University of Technology, **1998**; b) Y. Iwamoto, K. W. Völger, unpublished results.

[12] a) E. Kroke, A. O. Gabriel, R. Riedel, *Werkstoffwoche '98, Vol. 7*, Wiley-VCH, Weinheim, **1999**, p. 297; b) R. Riedel, A. O. Gabriel, *Adv. Mater.* **1999**, *11*, 207; c) K. W. Völger, Diploma Thesis, Darmstadt University of Technology, **1998**.

[13] R. Riedel, E. Kroke, A. Greiner, A. O. Gabriel, L. Ruwisch, J. Nicolich, P. Kroll, *Chem. Mater.* **1998**, *10*, 2964.

[14] a) A. O. Gabriel, E. Kroke, R. Riedel, unpublished results; b) J. S. Bradley, personal communication; c) R. T. Paine, personal communication.

[15] R. Rovai, C. W. Lehmann, J. S. Bradley, *Angew. Chem.* **1999**, *111*, 2073; *Angew. Chem. Int. Ed.* **1999**, *38*, 2036.

[16] M. Kawaguchi, *Adv. Mater.* **1997**, *9*, 615.

[17] R. Riedel, *Adv. Mater.* **1994**, *6*, 549.

[18] *Carbide, Nitride and Boride Materials Synthesis and Processing* (Ed.: A. W. Weimer), Chapman & Hall, London, **1997**.

[19] J. Weidlein, U. Müller, K. Dehnicke, *Schwingungsspektroskopie*, 2. Aufl., Thieme, Stuttgart, **1988**.

[20] See e.g.: a) H. Nozaki, S. Itoh, *J. Phys. Chem. Solids* **1996**, *57*, 41; b) R. Riedel, J. Bill, G. Passing, *Adv. Mater.* **1991**, *3*, 551; c) M. Kawaguchi, T. Kawashima, *J. Chem. Soc. Chem. Commun.* **1993**, 1133; d) V. L. Solozhenko, V. Z. Turkevich, T. Sato, *J. Am. Ceram. Soc.* **1997**, *80*, 3229.

[21] H. Nöth, H. Sachdev, H., *Z. Naturforsch. B* **1997**, *52*, 1345.

[22] I. A. Vostokov, Y. I. Dergunov, *Zh. Obshch. Khim.* **1977**, *47*, 1769.

Metallacoronates or One-Dimensional Polymers through Self-Assembly—Influence of Templates and Hydrogen Bonding on Product Formation[**]

Rolf W. Saalfrank,[*] Ingo Bernt, and Frank Hampel

Dedicated to Professor Dieter Sellmann
on the occasion of his 60th birthday

Design and synthesis of supramolecular inorganic structures with novel properties have provided exciting new possibilities.[1] We reported on the template-mediated self-assembly of six- and eight-membered iron coronates $[Na\subset Fe_6(L^1)_6]^+$ (**1**) and $[Cs\subset Fe_8(L^1)_8]^+$ (**2**).[2] They were prepared from triethanolamine (H_3L^1), iron(III) chloride, and sodium hydride or cesium carbonate, respectively (Scheme 1). A common feature of complexes **1** and **2** is that the ethanolato μ_1-O donors solely function as ligands for the coordinative saturation of the iron centers, whereas the ethanolato μ_2-O donors are structure-determining. Consequently, reaction of N-substituted diethanolamines **3** (H_2L^2)

---

[*] Prof. Dr. R. W. Saalfrank, Dr. I. Bernt, Dr. F. Hampel
Institut für Organische Chemie der Universität Erlangen-Nürnberg
Henkestrasse 42, 91054 Erlangen (Germany)
Fax: (+49) 9131-852-1165
E-mail: saalfrank@organik.uni-erlangen.de

[**] Chelate Complexes, Part 17. This work was supported by the Deutsche Forschungsgemeinschaft, the Bayerisches Langzeitprogramm "Neue Werkstoffe" and the Fonds der Chemischen Industrie. Part 16: R. W. Saalfrank, V. Seitz, F. W. Heinemann, C. Göbel, R. Herbst-Irmer, *J. Chem. Soc. Dalton Trans.* **2001**, 1–5.