Nitridic Ceramics

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Observation of Direct Bonds between Carbon and Nitrogen in Si-B-N-C Ceramic after Pyrolysis at 1400 °C**

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In recent years, the effect of the addition of carbon to various nitridic ceramics has been investigated. The quaternary amorphous ceramic SiBNC shows exceptional properties, such as excellent thermal stability and high resistance towards oxidative attack,[1,2] and they are promising candidates for industrial applications such as heat engines and turbines.[3,4] The properties are superior to those of $Si_3B_3N_7$,[5] therefore carbon seems to have a special role in this material. In most cases, pyrolysis above a given temperature leads to the formation of graphite-like domains.[6] However, such domains could not be detected with previous TEM and SEM studies in the case of SiBNC.[7] Using solid-state NMR spectroscopy in combination with a novel isotope labeling strategy, the presence of direct carbon–nitrogen bonds in the ceramic could be demonstrated for the first time. This is a remarkable result, since carbon–nitrogen bonds usually are unstable beyond 700 °C, but for the high-performance SiBNC ceramic seem to remain stable until at least 1400 °C. This finding may also shed some light on the potential stability of the still elusive β-C_3N_4.

A convenient way of producing SiBNC ceramics starts with the synthesis of a single-source precursor molecule (e.g. TADB, ($Cl_3Si(NH)BCl_2$)) and subsequent polymerization with methylamine.[8] This polymeric precursor can then be pyrolyzed under inert conditions to form SiBNC ceramic, which is stable in air. Obviously, the carbon in the SiBNC ceramic originates from the methyl group of methylamine. At the start of the pyrolysis process, carbon is connected to the network by a nitrogen bridge. In an earlier work, it was shown that the carbon–nitrogen bonds are still largely intact in the pre-ceramic stage of Si-B-N-C-H pyrolyzed at 600 °C.[9] Previous attempts to find carbon–nitrogen bonds in the fully pyrolyzed ceramic were unsuccessful.[10] In the present work, information about the bonds between carbon and nitrogen was obtained for the final ceramic pyrolyzed at 1400 °C by labeling both carbon and nitrogen atoms in methylamine with NMR-detectable isotopes (^{13}C and ^{15}N) and employing modern solid-state NMR methods.

In SiBN ceramics, nitrogen clearly functions as bridges between the other two atoms. To see whether the nitrogen atoms also form bridges to the carbon atoms in SiBNC ceramics, adiabatic cross-polarization (APHH-CP)[11] experiments were carried out. In the nitrogen spectrum obtained by cross-polarization from carbon, only those nitrogen nuclei that have carbon atoms in the direct vicinity contribute to the peak intensity, and vice versa. Such spectra were obtained for the sample pyrolyzed at 1400 °C and are shown in Figure 1. The fact that these spectra show a signal at all demonstrates that some of the carbon atoms are at close proximity to nitrogen atom and are possibly chemically bonded. The fact of these connections could be demonstrated only now and not before is most likely a consequence of the new isotope labeling scheme. Interestingly, this spectrum shows a higher intensity for the signal at $\delta = 141$ ppm relative to the signal at $\delta = 119$ ppm as compared with the spectrum resulting from direct excitation. In a previous work by van Wüllen et al.,[10] the proportion of carbon atoms that have a relatively close proximity to boron is somewhat higher for those that contribute to the signal at $\delta = 141$ ppm than for those corresponding to the signal at $\delta = 119$ ppm was demonstrated, and the presence of B-N-C bridges was hypothesized. These new experiments support this hypothesis. It should be noted, however, that CP is not a quantitative experiment.

Solid-state NMR spectroscopy allows the measurement of the dipolar coupling between spins, which is directly related to

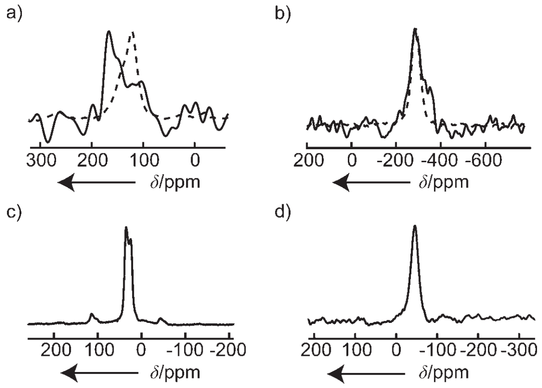

Figure 1. ^{13}C, ^{15}N, ^{11}B, and ^{29}Si spectra. a) ^{13}C Hahn echo (•••••, 1024 transients) and ^{15}N-^{13}C CP (——, 4904 transients, contact time 10 ms); b) ^{15}N Hahn echo (•••••, 64 transients) and ^{13}C-^{15}N CP (——, 1304 transients, contact time 10 ms); c) ^{11}B (64 transients); and d) ^{29}Si (4096 transients) NMR spectra of the final ceramic of $SiBN_3C$, $\omega_r/(2\pi) = 14$ kHz for Hahn echo and $\omega_r/(2\pi) = 25$ kHz for CP experiments.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

the internuclear distance. The distance between two heteronuclear spins can be determined by analyzing the degree of signal dephasing when applying the REDOR (rotational echo double resonance) pulse sequence.[12] The result of a ^{13}C{^{15}N} REDOR experiment is shown in Figure 2. Several different coordination environments of the carbon and nitrogen nuclei are possible in the investigated materials, therefore the experimental REDOR curve is compared with simulated REDOR curves for several different spin systems, generated with the simulation package SIMPSON.[13] Considering the limit value of the REDOR dephasing curve, roughly 80 % of the carbon nuclei seem to have a directly bonded nitrogen neighbor. This would correspond to most of the spectral component at $\delta = 141$ ppm and a large proportion of the component at $\delta = 119$ ppm. The simulated curves were corrected accordingly. A selection of these simulations is shown in Figure 2d; the rest are given in the Supporting Information. Dipolar couplings to nuclei other than ^{13}C and ^{15}N are averaged out under magic angle spinning and are assumed to have negligible influence. The REDOR curve matches the simulated curve of a carbon–nitrogen bond with some double bond character well. However, the experimental curve can be the result of a superposition of different configurations.

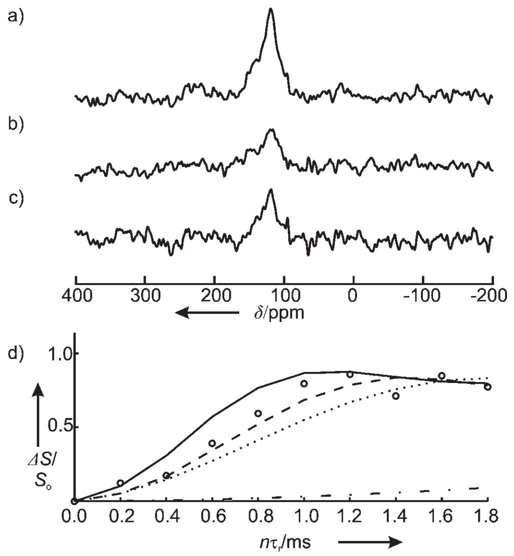

Figure 2. Experimental and simulated ^{13}C{^{15}N}REDOR curves (480 transients). $\omega_r/(2\pi) = 10$ kHz, $\Delta S/S_o$: normalized intensity difference, n: number of rotor cycles, τ_r: rotor period. a) ^{13}C Hahn echo MAS spectrum; b) ^{13}C{^{15}N}REDOR NMR spectrum at a dephasing time of 0.6 ms; c) difference spectrum d) experimental REDOR curve (○) and simulated REDOR curves with N=C=N (——, 1.34 Å, ∡120°), C=N (----, 1.34 Å), C–N (••••, 1.47 Å), and C–X–N (–•–•, 2.5 Å).

An alternative way of analyzing the REDOR curve is to compare the second moment (M_2) of the first few points of the experimental curve with the theoretical M_2 of chemically possible arrangements of carbon and nitrogen atoms. This analysis was performed by using the approach developed by Eckert and co-workers.[14,15] The advantage of the use of M_2 is that one can easily check whether a large number of nitrogen atoms without a direct bond to carbon could perhaps also account for the shape of the experimental REDOR curve. The results are shown in Figure 3. The observed value of M_2 (bar k) is significantly larger than that of any chemically relevant worst-case scenario of multispin interactions with no direct C–N bonds(bars i and j). The possibility of van der Waals contacts can also be ruled out (bars g and h). The experimental value of M_2 shows the best match with systems that have a carbon atom bonded to one or two nitrogen atoms with a bond order larger than 1 (bars c, d, and e).

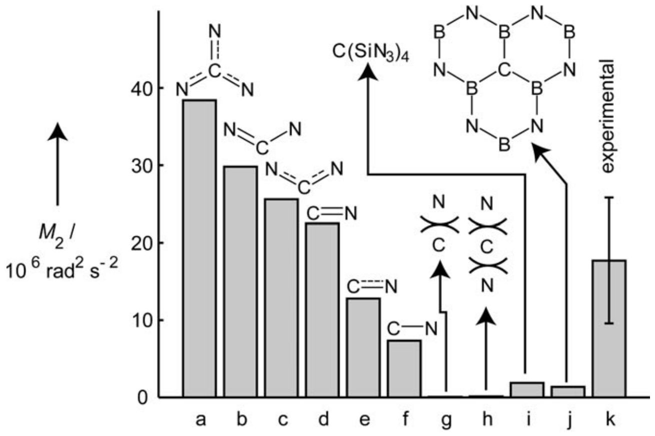

Figure 3. Second moment (M_2) analysis. a–f) Theoretical values for M_2 for a selection of directly bonded carbon–nitrogen systems. g,h) Theoretical values for M_2 for carbon–nitrogen systems separated by their van der Waals radii (3.2 Å). i,j) Theoretical values for M_2 for two worst-case scenarios: systems with multiple heteronuclear dipolar couplings over a two-bond distance. k) M_2 derived from the experimental REDOR curve. The size of the error bar is given by the difference of the values for M_2 as derived from the second and the third point of the REDOR curve.

Two important conclusions can be drawn from the REDOR data. First, as was stated before, a large proportion of the carbon remains connected to nitrogen in the final ceramic stage pyrolyzed at 1400 °C. Second, the carbon–nitrogen bond seems to have some π-bonding character. Meanwhile, the carbon signal appears in the sp^2 hybridized region of the spectrum. Some unsaturated carbon–carbon bonds are undoubtedly present, as was demonstrated previously[10,16] and confirmed in this work by ^{13}C-2D RFDR (Radio Frequency Driven Dipolar Recoupling) experiments[17] (see Figure 4), but the number of interconnected carbon atoms must be limited because of the high abundance of carbon–nitrogen bonds. Perhaps carbon atoms form small polycyclic aromatic segments bonded to the rest of the network by bridging nitrogen atoms. These nitrogen atoms participate in the π system of the aromatic segment, thus reducing the carbon–nitrogen bond length. An example of how the structure could appear on the atomic scale is shown in Figure 5. This structure includes all topologies identified in these and earlier experiments. Since the material is amorphous, NMR spectroscopy “sees” an average of all variations of the structural units that are present in the network.

For the first time, information could be obtained on how carbon is incorporated into the ceramic network of the final

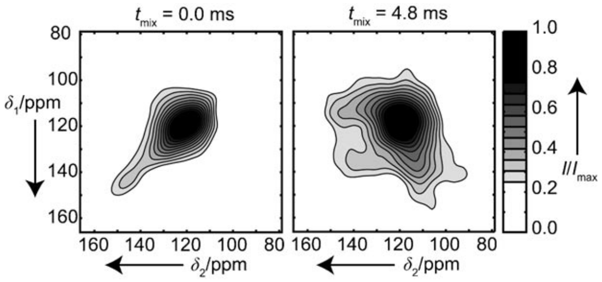

Figure 4. ^{13}C-2D RFDR spectra. ^{13}C homonuclear chemical shift–chemical shift correlation spectra recorded with the RFDR pulse sequence with a mixing time of 0 ms and 4.8 ms. The presence of off-diagonal intensity between the two components at $\delta = 119$ and 141 ppm demonstrates spatial proximity of the corresponding carbon species.

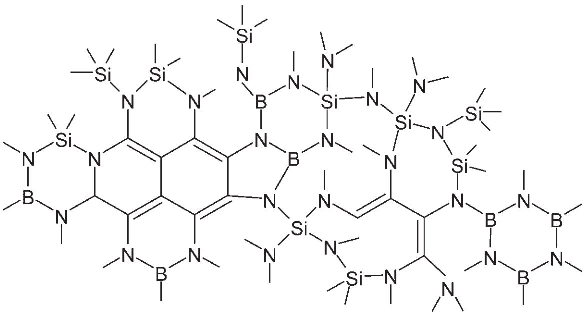

Figure 5. Proposed structure of SiBN$_3$C ceramic obtained by pyrolysis of TADB polymerized with methylamine. Carbon forms small polycyclic aromatic units that are connected with the rest of the structure mainly by nitrogen bridges.

quaternary ceramic SiBNC prepared from TADB and methylamine. As carbon seems to be involved into the network by nitrogen bridges, a nearly homogeneous arrangement of the elements is retained and the formation of a carbon-only domain is prevented. The presence of carbon–nitrogen bonds in this material is very surprising because these were thought to be unstable above 600 °C. This carbon–nitrogen bond is possibly stabilized at high temperatures by connecting with strong BN$_3$ and SiN$_4$ units in their vicinity (see Figure 5). This finding may be a vital clue for the superior stability against oxidation of SiBNC ceramics at elevated temperatures. Pondering the possible reasons why these connections between nitrogen and carbon have not been observed before may lead to new insights. Previously,[10] only the nitrogen atom of the TADB molecule was isotopically labeled, but obviously very few bonds from carbon to this particular nitrogen atom are created in the pyrolysis process. This result illustrates the very low diffusivity that the elements in this type of ceramic are known to have, and the necessity of using a polymeric precursor for its synthesis. Thus, knowing the structure of the ceramic provides important information for the optimization of the precursor system.

Experimental Section

Solid-state NMR experiments were performed on a Bruker DSX 400 spectrometer operating at a 9.4 T with 4 mm triple-resonance (HXY) probe for the Hahn-echo, REDOR, and with 2.5 mm double resonance probe for RFDR experiments. CP experiments were executed on Bruker AV 600 spectrometer (14 T) with 2.5 mm triple resonance probe. All experiments were performed at room temperature. Magic angle spinning frequencies were 10 kHz for REDOR, 7.5 kHz for RFDR, 14 kHz for the Hahn-echo experiments, and 25 kHz for the CP experiments. RF fields for REDOR were 23.8 kHz for ^{13}C and 25 kHz for ^{15}N and for CP were 75 kHz for ^{13}C and 50 kHz for ^{15}N. The chemical shifts are reported relative to tetramethylsilane (TMS), CH$_3$NO$_2$, BF$_3$·Et$_2$O, and TMS for ^{13}C, ^{15}N, ^{11}B, and ^{29}Si, respectively. The NMR data were processed with matNMR.[18] The experimental REDOR curve of the final ceramic is obtained by integrating the signal over the range from 120 to 150 ppm. Pulse sequences in this work are shown in Figure 3 in the Supporting Information.

An isotopically enriched sample of SiBN$_3$C ceramic was prepared from the single-molecule precursor TADB (Cl$_3$Si(NH)BCl$_2$) polymerized with 99 % ^{13}C, ^{15}N methylamine (Sigma Aldrich, ^{13}CH$_3$^{15}NH$_2$). All steps were performed under an argon atmosphere. The polymer was stirred for 8 h at 100 °C. The sample was heated up to 300 °C at a rate of 5 K min^{-1} followed by a dwell time of 5 h to complete polymer cross-linking. The sample was maintained for 5 h at 600 °C to decompose gas species completely. Subsequently, the pyrolysis temperature was raised to 900 °C at a rate of 5 K min^{-1} for another 3 h. The final ceramic was obtained by calcinating the pyrolyzed sample for 3 h in an alumina crucible at 1400 °C under an argon atmosphere.

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