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Short-Range Ordering in Amorphous $Si_3B_3N_7$ As Determined by Multinuclear NMR Spectroscopy

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IR and ^{29}Si, ^{11}B, and ^{15}N NMR-spectroscopic data of ^{15}N-enriched samples of hexamethyldisilazane, 1,1,1-trichloro-3,3,3-trimethyldisilazane (TTDS), 1,1,1-trichloro-3,3,3-trimethyldisilazane (TTDS), ((trichlorosilyl)amino)dichloroborane (TADB), of the poly(borosilazane) $Si_3B_3N_{7.9}H_{4.4}Cl_{0.8}O_{0.6}$, and of the ceramical network $Si_3B_3N_7$ are given. The ^{15}N-substituted samples have been prepared using novel synthetic routes. The NMR data show that in the poly(borosilazane) $Si_3B_3N_{7.9}H_{4.4}Cl_{0.8}O_{0.6}$ silicon is coordinated tetrahedrally by nitrogen in the first coordination sphere and boron is coordinated trigonally planar by nitrogen atoms. In this partially polymerized network, a small fraction of the nitrogen coordination is blocked by hydrogen, as verified by IR spectroscopy. Calcination of the poly(borosilazane) results in the fully polymerized network $Si_3B_3N_7$. The local coordination of silicon and boron remains virtually unchanged. As confirmed by comparison of the NMR data of $Si_3B_3N_7$ with those of crystalline references (Si_3N_4, BN), nitrogen is now fully coordinated by three silicon and/or boron atoms.

Introduction

The ternary and quaternary amorphous networks $Si_3B_3N_7$ and $SiBN_3C$ are high-performance ceramics with extraordinary mechanical and thermal properties, e.g. an excellent high-temperature resistance.[1−5] They are stable in an inert gas atmosphere up to 1700 °C ($Si_3B_3N_7$) and up to 1900 °C ($SiBN_3C$). Even their resistance to oxidation, usually a drawback of non-oxide ceramics, is the best known, so far.

To achieve the synthesis of materials with such outstanding properties, the use of molecular single-source precursors seems to be a crucial issue.[4] Ideally, the starting molecule should already contain part of the linkages as desired for the final ceramic, and these should survive during polymerization and pyrolysis, the usual processing sequence. All alternative approaches, e.g. via copolymerization or precursors with Si−B linkages different from those in the final solid,[6−8] have led to materials that undergo phase separations and crystallization on thermal loads.

Besides their potential as engineering materials, $Si_3B_3N_7$ and $SiBN_3C$ represent ideal random networks for studying the amorphous state of solid matters. The ceramics are amorphous showing no diffraction phenomena with either X-ray,[9] electron,[10] or neutron radiation.[9] The element distribution is found to be homogeneous down to a lateral resolution of 700 pm by electron scanning imaging.[10] Their compositions have been determined by chemical analysis.[11]

As a detailed knowledge of the microstructure of the systems under investigation is a principal prerequisite to understand their macroscopic chemical and physical properties, we have started to determine their structural features.

NMR spectroscopy is a powerful tool for probing the local environment of an atom in a solid lacking translational symmetry.[12] Among the constituting elements of $Si_3B_3N_7$, on which we will focus in this paper, silicon (^{29}Si) and boron (^{11}B) can be used in their natural abundance. Also, the prevailing isotope of natural nitrogen (^{14}N, $I = 1$) has been shown to be suitable for MAS NMR spectroscopy in principle.[13] However line-broadening, due to second-order quadrupolar interactions, reduces the sensitivity considerably and thus limits ^{14}N MAS NMR to samples with nitrogen in a highly symmetric surrounding. The nitrogen-15 nucleus with $I = {}^{1}/_{2}$ is problematic because of its low natural abundance of 0.4% and the long spin-lattice relaxation

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time in the range of 1 h. Cross-polarization (CP) from protons to enhance sensitivity is a well-established technique to overcome such problems.[14] In principle CP is also possible with proton-free substances as has been shown for hexagonal boron nitride where CP from boron-11 to nitrogen-15 could be realized.[15] Unfortunately the sensitivity of this method is not high enough to be applied to amorphous $Si_3B_3N_7$. Thus nitrogen-15 enrichment seemed to be inevitable.

In this paper we report on the short-range ordering in $Si_3B_3N_7$ as determined by IR and NMR spectroscopy. The measurements of the molecular precursor, the polymeric intermediate, and the fully pyrolyzed ceramic $Si_3B_3N_7$, with the constituting elements in their natural abundance, as well as partly or fully ^{15}N-substituted samples are discussed.

Experimental Section

All synthetic work was carried out in argon or nitrogen atmosphere using standard Schlenk techniques.

IR spectra were recorded on a Fourier transform infrared spectrometer Bruker IFS 113v. In the MIR range a globar was used as light source. The transmission was registered by a mercury cadmium telluride photodetector. Liquid samples were deposited in a cuvette with KBr windows and measured at 20 °C. Solids were mixed with KBr and pressed to pellets.

Solution NMR spectra were recorded on a Bruker AMX 300 spectrometer. For ^{15}N measurements the chemical shifts were referenced to nitromethane.

All solid-state ^{29}Si, ^{11}B, and ^{15}N NMR spectra were recorded on a Varian Unity 400 spectrometer ($B_0 = 9.4$ T) at 79.2, 127.9, and 40.4 MHz, respectively. High-resolution solid-state NMR spectra were collected using magic angle spinning (MAS) with a 5 mm standard Doty probe and zirconia rotors. Single-pulse acquisition was used with a recycle delay of $5T_1$ to avoid saturation effects. Samples were spun at 8 kHz for ^{29}Si, 12 kHz for ^{11}B, and 10 kHz for ^{15}N spectroscopy. The ^{29}Si spectra were recorded with recycle delays up to 900 s to ensure a complete relaxation; 200 free induction decays (FID's) were averaged to obtain each ^{29}Si MAS spectrum. The ^{11}B spectra with 200 accumulated transients were collected using non-selective pulses with a 1 μs 15° pulse and a 30 s recycle delay. The ^{15}N pulse delays between acquisitions were 600 s, and up to 560 transients (depending on the degree of ^{15}N enrichment) were accumulated. The spectral width was set to 100 kHz, the acquisition time was 33 ms, and a 100 Hz exponential line broadening was applied during data processing for ^{29}Si- and ^{15}N-MAS spectra. No smoothing was necessary in data processing of the ^{11}B MAS spectra.

The mean error of the measured chemical shifts (peak maxima) is estimated to amount to ±1 ppm. The ^{29}Si chemical shift reference was TMS (tetramethylsilane), the ^{11}B chemical shifts were measured versus BF_3OEt_2, and ^{15}N data were referenced to solid NH_4Cl, which is shifted by −338.2 ppm relative to nitromethane, another common ^{15}N reference material.[16]

Materials. ^{15}N-ammonia (99% ^{15}N) and ^{11}B-boric acid (99% ^{11}B) were purchased from Cambridge Isotope Laboratories. Trimethylchlorosilazane, silicon tetrachloride, and boron trichloride obtained from Fluka were purified by distillation.

Preparation of ^{15}N-Hexamethyldisilazane (HMDS). Liquid ammonia (132 mmol, 3.7 mL) is allowed to evaporate to a refluxing mixture of trimethylchlorosilane (88 mmol, 12.24 mL) in 100 mL of diethyl ether over a period of 4 h. The ammonium chloride formed during the reaction is filtered off. The diethyl ether is distilled off at reduced pressure, and the yield of hexamethyldisilazane is 70% related to ammonia.

Table 1. Assignment of IR Data for HMDS and Comparison of the Natural and the ^{15}N Isotopomers

	ν(N−H)	ν_{as}(CH_3)	ν_s(CH_3)	δ_{as}(CH_3)	δ_s(CH_3)	δ_{as}(SiNH)
nat. HMDS	3381	2957	2899	1442	1253	1182
^{15}N-HMDS	3374	2957	2899	1441	1254	1174

	ν_{as}(Si_2N)	ρ_{as}(CH_3)	ρ_s(CH_3)	ν_{as}(SiC_3)	ν_s(SiC_3)	ν_s(Si_2N)
nat. HMDS	934	841	756	685	618	567
^{15}N-HMDS	916	843	755	685	618	558

IR: see Table 1. ^{15}N NMR (C_6D_6): $\delta = 353.0$ ppm (s).

Preparation of ^{15}N-1,1,1-Trichloro-3,3,3-trimethyldisilazane (TTDS). A mixture of silicon tetrachloride (60 mmol, 10.2 g) and ^{15}N-hexamethyldisilazane (30 mmol, 4.9 g) is stirred at room temperature for 24 h. Subsequent distillation at 15 mbar, 45 °C, yields 90% TTDS.

IR: see Table 2. ^{15}N NMR (C_6D_6): $\delta = 329.8$ ppm (s).

Preparation of ^{11}B-Trichloroborane. ^{11}B-boric acid (0.4 mol, 25 g) is heated at 200 °C for 2 days over phosphorus pentoxide to get boron oxide. The powdered boron oxide is heated with phenol (1.3 mol, 121 g) for 3 days at 160 °C. The excess of phenol is removed by distillation at 200 °C and 15 mbar. A mixture of the triphenyl orthoborate and aluminum chloride is heated with a Bunsen burner. The resulting trichloroborane is collected in a cooling trap at −78 °C and purified by subsequent condensation through a sequence of three cooling traps. Yield: 60%.

Preparation of ^{15}N- and/or ^{11}B-((Trichlorosilyl)amino)dichloroborane (TADB). Reaction of TTDS (13 mmol, 3.0 g) with boron trichloride (27 mmol, 3.2 g) at −78 °C for 12 h leads to the target molecule. Distillation at 14 mbar, 37 °C, yields 90% TADB.

IR: see Table 3. ^{15}N NMR (C_6D_6): $\delta = 273.8$ ppm (broad signal).

Preparation of ^{15}N- and/or ^{11}B-Poly(borosilazane) $Si_3B_3N_{7.9}H_{4.4}Cl_{0.8}O_{0.6}$. In the sample referred to as **a** the ammonia used for cross linking is enriched with 20% nitrogen-15. Sample **b** is prepared from fully nitrogen-15-substituted TADB. Sample **c** is 100% enriched with nitrogen-15 and boron-11.

TADB (14 mmol, 3.2 g) dissolved in 25 mL of pentane (280 mmol of NH_3, 7.4 mL) is added dropwise to liquid ammonia at −78 °C under vigorous stirring. The reaction mixture is allowed to warm to room temperature overnight. The pentane is distilled off at reduced pressure.

The colorless powder is heated in flowing argon atmosphere to 400 °C at 250 K/h, to 500 °C at 25 K/h, held for 2 h, and then cooled to room temperature at 150 K/h. The ammonium chloride formed as a byproduct during the cross-linking is now removed by evaporation.

Composition (commercial analysis, Pascher Remagen, Germany): Si 30.4%, B 11.7%, N 40.6%, H 1.60%, Cl 11.1%, and O 3.47%, leading to the formula $Si_3B_3N_{7.9}H_{4.4}Cl_{0.8}O_{0.6}$.

Preparation of ^{15}*N*- and/or ^{11}*B*-$Si_3B_3N_7$. To get the final ceramic the poly(borosilazane) is heated to 1400 °C at 30 K/h, held for 6 h, and cooled to room temperature at 30 K/h in flowing nitrogen.

Results and Discussion

Preparation of the Samples. The synthesis of $Si_3B_3N_7$ and its evolution through the polymeric states has been described elsewhere.[17] The synthetic procedure (Figure 1) offers two options for introducing ^{15}N, either during the synthesis of the molecular precursor ((trichlorosilyl)amino)dichloroborane (TADB) or at its aminolysis and polycondensation by reaction with ammonia

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Table 2. Assignment of IR Data for TTDS and Comparison of the Natural and the ^{15}N Isotopomers

	ν(N−H)	$\nu_{as}(CH_3)$	$\nu_s(CH_3)$	$\delta_{as}(CH_3)$	$\delta_s(CH_3)$	δ_{as}(SiNH)	$\nu_{as}(Si_2N)$
nat. TTDS	3367	2961	2901	1412 w	1256	1188	972
^{15}N-TTDS	3362	2961	2902	1408	1256	1178	957

	$\rho_{as}(CH_3)$	$\rho_s(CH_3)$	$\nu_s(Si_2N)$	$\nu_s(SiC_3)$	$\nu_{as}(SiCl_3)$	$\nu_s(SiCl_3)$
nat. TTDS	845	766 s	689	608	577	463
^{15}N-TTDS	846	762	684	605	577	459

Table 3. Assignment of IR Data for TADB and Comparison of the ^{11}B and ^{15}N Isotopomers with the Calculated Bands

	ν(N−H)	$\nu(^{10}B{-}N)$	$\nu(^{11}B{-}N)$	δ_{as}(B−N−H)	$\nu_{as}(^{10}BCl_2)$
nat. TADB	3366	1372	1349	1223	950
^{11}B-TADB	3367		1350	1222	
^{15}N-^{11}B-TADB	3360		1338	1218	
calcd $^{11}B^{14}N$-TADB	3466		1369	1187	
calcd $^{10}B^{14}N$-TADB	3466	1400		1205	982
calcd $^{11}B^{15}N$-TADB	3458		1348	1185	

	$\nu_{as}(^{11}BCl_2)$	ν(Si−N)	τ(ClSiN)	$\nu_s(BCl_2)$	$\nu_s(SiCl_3)$
nat. TADB	921	855	616	564	484
$^{11}B^{nat}N$-TADB	922	855	618	564	484
$^{11}B^{15}N$-TADB	921	844	618	555	480
calcd $^{11}B^{14}N$-TADB	950	861	645	572	485
calcd $^{10}B^{14}N$-TADB		865	646	575	*a*
calcd $^{15}N^{11}B$-TADB	950	849	645	565	*a*

[a] Not given in ref 25.

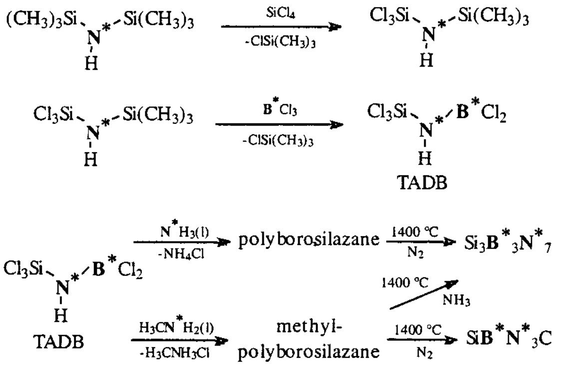

Figure 1. Synthesis of TADB, $Si_3B_3N_7$, and $SiBN_3C$. Atoms to be enriched by the appropriate isotopes are marked with asterisks.

or methylamine. Due to the very high price of ^{15}N-methylamine, ^{15}N-ammonia was used for the cross-linking of TADB. Overall, four different types of samples have been prepared. Two with boron in natural abundance, however, ^{15}N substituted either in TADB or by cross-linking with $^{15}NH_3$. The two remaining types contained ^{11}B (100%), needed for neutron diffraction[9], and nitrogen, either in natural abundance or fully substituted by ^{15}N.

To reduce losses of the expensive isotope-enriched starting materials, the previously reported syntheses of the intermediates HMDS and trichloroborane[18,19] (cf. Figure 1) have been modified and optimized.

Infrared Spectroscopy. The IR spectrum of HMDS has been discussed by several authors.[20−22] The assignments as taken from the literature and the wavenumbers of the two isotopomers are given in Table 1. Assuming an almost free rotation of the trimethylsilyl group, we can assign C_{2v} symmetry to the molecule as a whole and C_{3v} symmetry to the trimethylsilyl group. For comparison of the wavenumbers of the isotopomers, it can be concluded that the vibrations of the Si−N−Si backbone and those of the trimethylsilyl groups are virtually independent of each other. An isotopic shift is observed exclusively for bands related to vibrations involving nitrogen, i.e., vibrations of the Si−N−Si backbone.

No IR spectroscopic studies of TTDS have been reported so far. The interpretation of this spectrum is more difficult since strong coupling between the vibrations of the Si−N−Si backbone and the inner vibrations of the trichlorosilyl group are expected due to the relatively high mass of the chlorine atoms. By comparing the data of the two nitrogen isotopomers with the spectra of HMDS, hexachlorodisilazane,[23] and 1,1,1,2-tetrachlorodisilazane,[24] we have derived a reasonable assignment, given in Table 2. The assignment of the vibrations of the trimethylsilyl group is evident, and its most characteristic bands $\rho_{as}(CH_3)$ and $\delta_s(CH_3)$ do not show any isotopic shift. The other group frequencies assigned as $\delta_{as}(CH_3)$, $\rho_s(CH_3)$, and $\nu_s(SiC_3)$ show small isotopic shifts to lower wavenumbers caused by coupling with the stretching vibration frequencies of the Si−N−Si unit. The $\nu_s(SiCl_3)$ vibration is coupled with $\nu_s(Si_2N)$ as it has been reported for hexachlorodisilazane.[23] $\nu_{as}(Si_2N)$ of TTDS is at higher values than in HMDS, following a general trend, found in disilazanes, when methyl groups are substituted by halogen atoms.[23]

On the basis of local density functional calculations, the IR data for TADB have been discussed and the assignments of the bands and the comparison of the calculated with the measured IR spectra has been given there in detail.[25] The calculated frequencies and the measured ones of the different ^{15}N and ^{11}B isotopomers

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Table 4. NMR Spectroscopic Data for the Crystalline Reference Compounds, Polymers, and Ceramics

compound	^{29}Si δ_{iso}/ppm	11B δ_{iso}/ppm	11B C_Q/MHz	11B η	15N δ_{iso}/ppm
hex. BN		30.0(5)	2.90(5)	0.0	63
α-Si_3N_4	−46.1, −48.2				29.7, 31.5, 42.1, 54.2
β-Si_3N_4	−48.7[26]				32.2, 49.4
polymers **a** and **b**	−38.9 to −40.1; fwhm 1.3 kHz	29(1)	2.8(1)	0.0 to 0.1	42.7−0.43.5; fwhm 2.2−2.5 kHz
ceramics **a**−**c**	−45.0 to −48.2; fwhm 2.0 kHz	30(1)	2.9(1)	0.0 to 0.1	55.9−60.1; fwhm 1.5−1.6 kHz

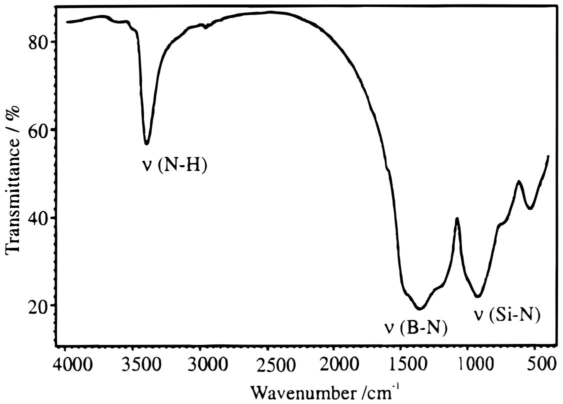

Figure 2. IR spectrum of the polyborosilazane heated to 500 °C.

are shown in Table 3. By the data presented here, the calculated isotopic shifts can be verified experimentally. The difference between the stretching vibrations $\nu(^{11}B-^{14}N)$ and $\nu(^{11}B-^{15}N)$ is found to be 12 cm^{-1}, while the calculated value is 21 cm^{-1}. The corresponding shift for the δ_{as}(B−N−H) bending vibration is 4 cm^{-1}, and the predicted value is 2 cm^{-1}. The isotopic shift of the ν(Si−N) vibration of 11 cm^{-1} is calculated to be 12 cm^{-1}. The $\nu_s(BCl_2)$ stretching mode is coupled to the ν(B−N) stretching leading to an isotopic shift of 9 cm^{-1} (calculated 7 cm^{-1}). Thus the calculated isotopic shifts are in a good agreement with the values found experimentally.

The IR spectrum of the poly(borosilazane) $Si_3B_3N_{7.9}H_{4.4}Cl_{0.8}O_{0.6}$, as obtained by cross-linking of TADB with ammonia and subsequent thermal treatment up to 500 °C, is given in Figure 2. It shows very broad bands which can be assigned to boron−nitrogen (1353 cm^{-1}) and silicon−nitrogen (922 cm^{-1}) stretching vibrations. The absorption at 3398 cm^{-1} is related to the nitrogen−hydrogen stretching vibration. These results are compatible with those found for the methyl−poly(borosilazane) as obtained from the cross-linking of TADB with methylamine.[17]

The IR spectrum of the fully pyrolyzed ceramic $Si_3B_3N_7$ shows two very broad absorptions covering characteristic ranges of the boron−nitrogen (1384 cm^{-1}) and silicon−nitrogen (983 cm^{-1}) stretching vibrations.

Silicon-29 NMR Spectroscopy. The ^{29}Si MAS NMR spectra of the polymers, $Si_3B_3N_{7.9}H_{4.4}Cl_{0.8}O_{0.6}$, **a** and **b** show a broad peak at about −40 ppm (Table 4) with a halfwidth of 1.3 kHz. Figure 3 displays the ^{29}Si MAS NMR spectra of $Si_3B_3N_7$ with signals at about −45 ppm and the spectrum of α-Si_3N_4. This spectrum displays two ^{29}Si signals at −47.1 and −48.6 ppm (Table 4) according to the two different crystallographic sites of the silicon atoms and is in agreement with a previous work of Carduner et al.[26] By comparison the ^{29}Si signals of the polymer and of the ceramic can be ascribed to tetrahedrally coordinated silicon. The large peak width suggests a broad distribution of differently distorted SiN_4 tetrahedra.

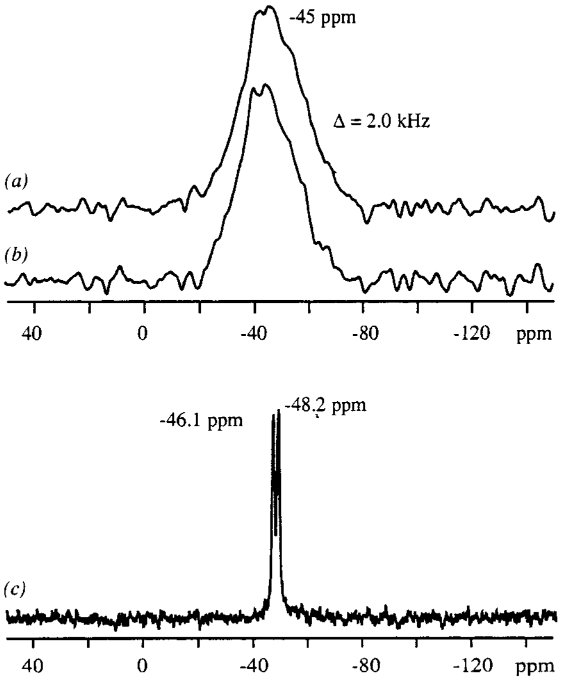

Figure 3. ^{29}Si MAS NMR spectra of (a) sample **a** of $Si_3B_3N_7$, (b) sample **b** of $Si_3B_3N_7$, and (c) α-Si_3N_4.

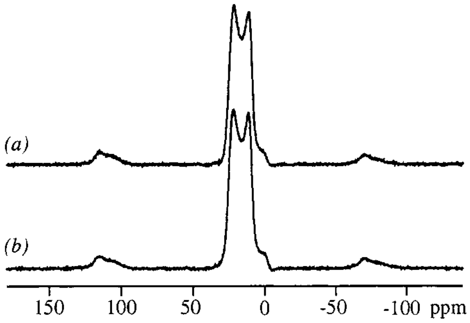

Figure 4. ^{11}B MAS NMR spectra of $Si_3B_3N_{7.9}H_{4.4}Cl_{0.8}O_{0.6}$: (a) sample **a**; (b) sample **b**.

Boron-11 NMR Spectroscopy. The ^{11}B spectra of the two polymers **a** and **b** (Figure 4) closely resemble that of hexagonal boron nitride.[15] Beyond that the spectra of the ceramic (Figure 5) and of hexagonal boron nitride are virtually identical regarding line shape as well as chemical shift. The signals are clearly different from those typical for tetrahedrally coordinated boron in e.g. cubic boron nitride, where the first-order quadrupolar interaction produces a rather narrow (150 Hz) single resonance at −1.6 ppm.[27] The line shapes of the

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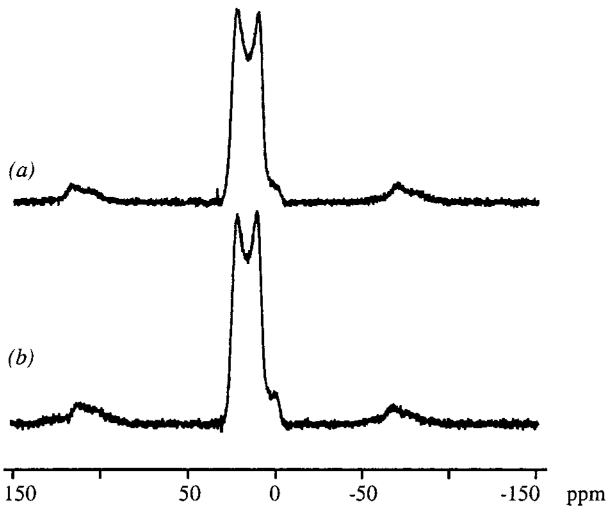

Figure 5. ^{11}B MAS NMR spectra of $Si_3B_3N_7$: (a) sample **a**; (b) sample **b**.

spectra of the polymer and the ceramic are characteristic for strong second-order quadrupolar interactions of an $I = {}^{3}/_{2}$ nuclide. By the MAS technique second-order effects are partially removed, a residual broadening arises from the $P_4(\cos\,\theta)$ term.[28] Only the central transition and its spinning sidebands are observed. Since the ^{11}B-MAS line shape is strongly dependent on the local coordination geometry, this implies a virtual identical coordination of boron in the polymer and the reference compound (trigonal planar by three nitrogen). The ^{11}B-MAS spectrum of $Si_3B_3N_7$ has been simulated. The resulting values for the quadrupole coupling constant (C_Q) and the electric field gradient asymmetry parameter η (see Table 4) are in good agreement with those of hexagonal boron nitride reported by Silver and Bray[29] and confirmed previously by NQR at low temperature.[30] The virtual identity of the ^{11}B-MAS spectrum of $Si_3B_3N_7$ and hexagonal boron nitride proves that in the ceramic boron is in a fairly regular trigonal planar environment. Additional support for the given interpretations comes from double rotation (DOR)[31] data for $Si_3B_3N_7$ and hexagonal boron nitride. Again the spectra are very similar exhibiting almost identical isotropic shift and line shape.[32]

Nitrogen-15 NMR Spectroscopy. The ^{15}N MAS NMR spectra of the two polymers show a peak at 42.4 for **a** and 42.2 ppm for **b** (Table 4), with a halfwidth of 2.0 kHz, thus at considerably higher field in comparison with the signal at about 60 ppm of the fully pyrolyzed ceramic (Figure 6). As references we use the ^{15}N-MAS spectra of α-Si_3N_4 (four peaks at 29.7, 31.5, 42.1, and 54.2 ppm) and β-Si_3N_4 (two peaks at 32.2 and 49.4 ppm)[33] and the recent ^{14}N MAS measurements on cubic and hexagonal BN with an isotropic chemical shift at -18 and 63 ppm, respectively.[13,15] The chemical shift of hexagonal BN has been predicted by calculations to be 53 ± 5 ppm.[34] Since the existence of nitrogen–hydrogen bonds in the polymer is verified by IR spectroscopy (see above), we tentatively assign the chemical shift of about 42 ppm to nitrogen being coordinated by one (or even two) hydrogen atom(s) and two (or one) further silicon and/or boron atom(s). The spectra of the ceramics **a**–**c** given in Figure 6 show broad signals at 60, 56, and 59 ppm. The halfwidth in all spectra is about 1.5 kHz. The isotropic chemical shifts of hexagonal boron nitride and all respective signals of silicon nitride fall within the wide range covered by the signal, as recorded for $Si_3B_3N_7$. So, there is clear evidence that the nitrogen atoms are coordinated trigonally planar by silicon and boron. However distinguishing between the different coordinations NSi_3, NSi_2B, $NSiB_2$, and NB_3 is not yet possible.

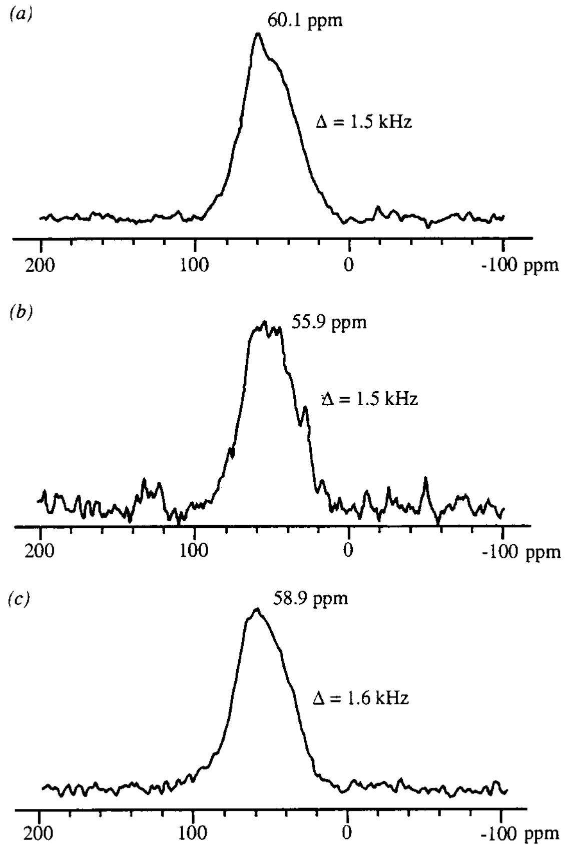

Figure 6. ^{15}N MAS NMR spectra of ^{15}N-enriched $Si_3B_3N_7$: (a) sample **a**; (b) sample **b**; (c) sample **c**.

Conclusion

By recording the MAS NMR spectra of all atoms constituting the random network $Si_3B_3{}^{15}N_7$ and comparing them with suitable crystalline references (Si_3N_4, BN), we have determined unambiguously their short-range order. Silicon is coordinated tetrahedrally and boron trigonally planar by nitrogen, while nitrogen is exclusively coordinated by three silicon and/or boron atoms. The different combinations $NSi_{3-x}B_x$ ($x = 0-3$) could not be resolved. The ^{29}Si signal for $Si_3B_3N_7$ is extremely broad, indicating a large distribution of the Si–N bond lengths and/or the N–Si–N bond angles of

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the SiN_4 tetrahedra. As the variations in the next-neighbor Si−N and B−N separations are rather small according to the results of X-ray,[9] electron,[10] and neutron[9] diffraction, the line broadening can be attributed mainly to angular distortions. As the BN_3 units are rather rigid, the deformations, a necessary response to the inevitable elastic strain within a random network, seem to accumulate in the least rigid structural feature, the Si−N−Si angles.

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