Understanding Intermediate-Range Order in Amorphous Nitridic Ceramics: A $^{29}Si\{^{11}B\}$ REDOR/REAPDOR and $^{11}B\{^{29}Si\}$ REDOR Study

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The structural organization of nitridic ceramics in the system Si/B/N/C on an intermediate length scale is studied using $^{29}Si\{^{11}B\}$ rotational echo adiabatic passage double resonance (REAPDOR) and $^{11}B\{^{29}Si\}$ rotational echo double resonance (REDOR) NMR spectroscopy. The experiments are performed on a 100% ^{29}Si enriched $^{29}Si_3B_3N_7$ ceramic material, obtained by ammonolysis and subsequent pyrolysis of the single-source precursor molecule ((trichlorosilyl)amino)dichloroborane (TADB, $Cl_3{}^{29}SiNHBCl_2$). Simulations of the resulting double resonance curves on the basis of multiple spin interactions are presented. The double resonance data is supported by additional ^{11}B and ^{29}Si static dipolar spin−echo experiments. The combined results obtained from the different experimental approaches indicate an unexpected connectivity motif in these ceramics, characterized by regions of mainly Si−N−Si linkages and islands of predominantly B−N−B connectivities.

Introduction

Amorphous ceramic materials in the system B/C/N/Si have gained considerable importance as high-performance materials due to their fascinating thermal and mechanical properties.[1,2] Among these materials, those obtained by polycondensation and subsequent pyrolysis of molecular single-source precursors exhibit an improved resistance to phase separation and crystallization during the pyrolysis process,[3] and their resistance to oxidation is unprecedented among the non-oxidic ceramic materials.[4,5] The structural characterization of these amorphous networks is a prerequisite for an understanding of the chemical and physical properties of these materials and the fine-tuning thereof. A lot of effort has been put into the characterization of these materials, among these especially the ternary $Si_3B_3N_7$ and the quaternary $SiBN_3C$. While the short range order has been studied successfully using standard MAS NMR techniques[6] (^{29}Si, ^{11}B, ^{15}N), XANES spectroscopy,[7] and X-ray and neutron diffraction techniques[8] revealing BN_3 and SiN_4 units as the polyhedra constituting the network, the ordering on a distance scale down to 9 Å has been accessed by means of energy-filtered transmission electron spectroscopy (EFTEM) and electron spectroscopic imaging (ESI).[9] These studies found that the ceramics $Si_3B_3N_7$ and $SiBN_3C$ are homogeneous with respect to the elemental distribution on a subnanometer scale. However, the important intermediate-range (2−6 Å) ordering of the network-forming polyhedra SiN_4 and BN_3 has not yet been accessible.

Double resonance NMR techniques have proven to be a powerful tool for the characterization of intermediate-range ordering phenomena in amorphous solids. These techniques utilize the dipole−dipole coupling strength between two nuclear spins I and S to obtain information about $I-S$ internuclear distances. While the rotational echo double resonance (REDOR)[10−14] approach works well if the dephasing nucleus is a $I = {}^1/_2$ nucleus, the method works only insufficiently for quadrupolar ($I > {}^1/_2$) nuclei, since only spin populations in the central transition contribute to the dephasing, thus severely complicating data analysis. In these cases, transfer of populations in double resonance (TRAPDOR)[15−19] and rotational echo adiabatic passage double resonance

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(REAPDOR)[20–22] spectroscopy have been shown to overcome the shortcomings of REDOR.

In the present study, we use ^{29}Si{^{11}B} REDOR and REAPDOR spectroscopy to study the intermediate range order in the ceramic $Si_3B_3N_7$ and discuss an analysis of the obtained REDOR and REAPDOR curves on the basis of single and multiple spin interactions. The reverse experiment—^{11}B{^{29}Si} REDOR—is hampered by the low natural abundance (4.7%) of the ^{29}Si isotope but would be highly desirable as a second source of information for the intermediate-range order in these ceramics. We therefore used a 100% ^{29}Si-enriched sample of $Si_3B_3N_7$ for our experiments. Finally, we will present ^{11}B and ^{29}Si static dipolar spin−echo NMR experiments which measure the homonuclear dipolar couplings, thus exploring homonuclear intermediate-range order. Analysis of these experiments supports the findings concluded from the double resonance data.

Experimental Section

The 100% ^{29}Si-enriched $Si_3B_3N_7$ sample was synthesized as follows: ^{29}Si was reacted with lead(II) chloride ($PbCl_2$, Fluka) to $^{29}SiCl_4$. $^{29}SiCl_4$ was then added to hexamethyldisilazane ($Me_3SiNHSiMe_3$, Fluka) to give 1,1,1-trichloro-3,3,3-trimethyldisilazane, which then was reacted with boron trichloride (BCl_3, Fluka), resulting in the desired single source precursor molecule ((trichlorosilyl)amino)dichloroborane (TADB). Ammonolysis and polycondensation was achieved by addition of liquid ammonia. Ammonium chloride as a byproduct was removed by sublimation at 500 °C prior to pyrolysis at 1400 °C.

All NMR experiments were performed on a Bruker DSX 400 spectrometer operating at 9.4 T using a 4-mm triple resonance (H XY) probe. The resonance frequencies were 79.46 and 128.33 MHz, respectively. All spectra were recorded at spinning speeds of 5−10 kHz. Rf fields were set to 29.4 kHz for ^{29}Si and 48−89 kHz for ^{11}B, corresponding to $\pi/2$ (liquid) values of 8.5 μs and 2.8−5.2 μs for ^{29}Si and ^{11}B, respectively.

Figure 1 shows the pulse sequences used in this work. In REDOR (Figure 1a), the reintroduction of the heteronuclear dipolar couplings, normally averaged out under the conditions of MAS, is accomplished by introducing rotor-synchronized π-pulses for the dephasing (I) nucleus. Among the various REDOR versions, the sequence using a conventional rotor-synchronized spin−echo on the observe channel (S) was applied. REAPDOR, a combination of REDOR and TRAPDOR, was designed for optimal performance when the dephasing nucleus (I) is a half-integer quadrupolar nucleus. In this experiment, the reintroduction of the heteronuclear dipolar coupling is achieved by an adiabatic rf pulse in the middle of the pulse sequence (Figure 1b). The length of the dephasing pulse was set to one-third of the rotation period.

Results

Typical ^{11}B{^{29}Si} REDOR and ^{29}Si{^{11}B} REAPDOR spectra are plotted in Figure 2. The ^{11}B line shape is indicative of a second-order quadrupolar powder pattern (C_Q = 2.9 MHz; η = 0.1). The top spectra represent results of ^{11}B (Figure 2a) and ^{29}Si (Figure 2b) MAS spin−echo experiments defining the corresponding reference intensity S_0; middle spectra were obtained by applying the REDOR (Figure 1a) and REAPDOR (Figure 1b) sequence giving the decreased echo amplitude S, while the bottom spectra represent difference intensities. The magnitude of the normalized difference signal $(S_0 - S)/S_0$ depends both on the strength of the dipolar coupling and the length of the dipolar evolution time NT_R, T_R being the rotor period and N the number of

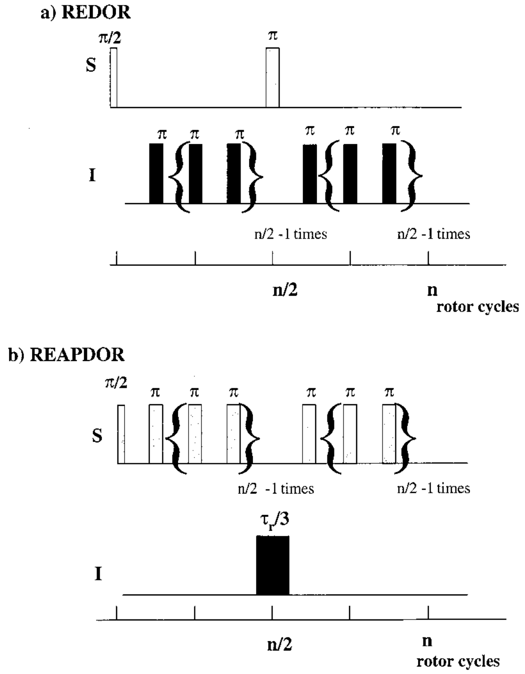

Figure 1. Pulse sequences used in this work: (a) REDOR; (b) REAPDOR.

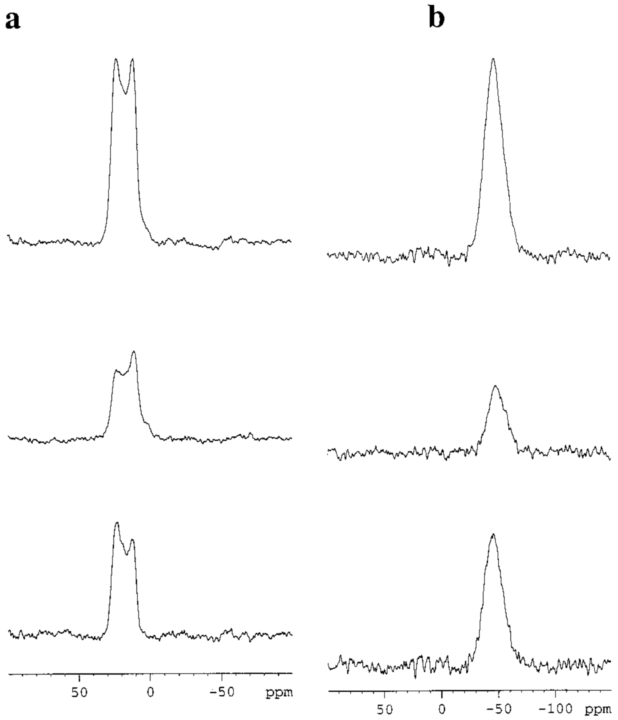

Figure 2. Typical ^{11}B{^{29}Si} REDOR and ^{29}Si{^{11}B} REAPDOR spectra for the studied $Si_3B_3N_7$ ceramic. Experimental details: $\nu_{RF}(^{29}Si)$ = 29.4 kHz; $\nu_{RF}(^{11}B)$ = 89 kHz; ν_{MAS} = 10 kHz (REDOR) and 5 kHz (REAPDOR). Spectra: top, ^{11}B (left) and ^{29}Si (right) MAS spin−echo spectra; middle, ^{11}B{^{29}Si} REDOR (left) and ^{29}Si{^{11}B} REAPDOR (right) spectra; bottom, REDOR and REAPDOR difference spectra.

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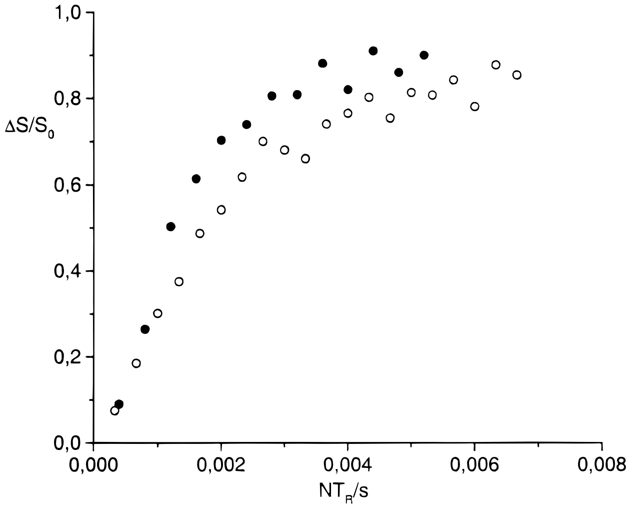

Figure 3. Experimental ^{29}Si{^{11}B} REAPDOR curves for $\nu_{MAS} = 5$ kHz, $\nu_{RF}(^{11}B) = 89$ kHz (filled circles) and $\nu_{MAS} = 6$ kHz, $\nu_{RF}(^{11}B) = 48$ kHz (open circles). $\nu_{RF}(^{29}Si) = 29.4$ kHz in both experiments.

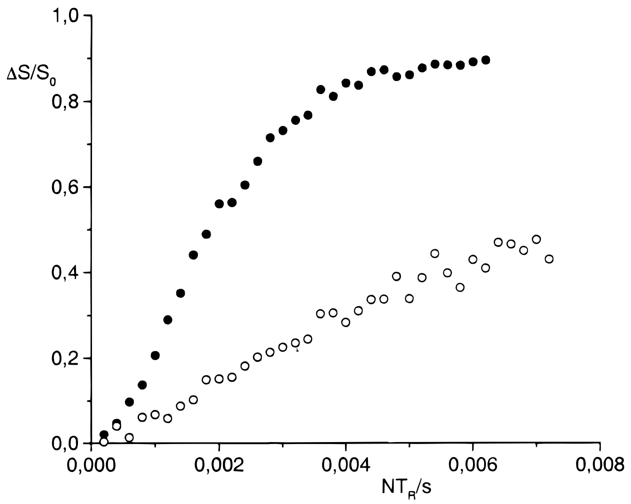

Figure 4. Experimental ^{29}Si{^{11}B} REDOR (open circles) and ^{11}B{^{29}Si} REDOR (filled circles) dephasing curves for $^{29}Si_3B_3N_7$: $\nu_{MAS} = 5$ kHz; $\nu_{RF}(^{11}B) = 89$ kHz; $\nu_{RF}(^{29}Si) = 29.4$ kHz.

rotor cycles. The resulting ^{11}B{^{29}Si} REDOR, ^{29}Si{^{11}B} REDOR and REAPDOR curves, each obtained by plotting the MAS echo difference signal amplitudes $\Delta S/S_0$ as a function of the dipolar evolution time NT_R, are shown in Figures 3 and 4. Figure 3 shows the results of two different ^{29}Si{^{11}B} REAPDOR experiments on $Si_3B_3N_7$. Solid circles correspond to experimental conditions $\nu_{MAS} = 5$ kHz and $\nu_{RF} = 89$ kHz, and open circles to an experiment performed with $\nu_{MAS} = 6$ kHz and $\nu_{RF} = 48$ kHz. Note that REAPDOR difference intensities are higher for the experiment with the higher ^{11}B RF field and lower MAS frequency. This observation is confirmed by additional data (not shown) and is a manifestation of the dependence of the dephasing efficiency on the adiabaticity parameter $\alpha = \nu^2_{RF}/\nu_Q\nu_{MAS}$ introduced by Vega.[23]

The main characteristic of the ^{29}Si{^{11}B} REDOR curve (Figure 4; open circles) is a leveling off at a $\Delta S/S_0$ value near 0.5. A comparison with the REAPDOR curves in Figure 3 confirms the superior dephasing characteristic of the REAPDOR pulse sequence relative to REDOR. Since in the REAPDOR experiment principally all spin states of a quadrupolar nucleus are involved in dipolar dephasing, the dephasing is much more efficient than in the corresponding REDOR experiment, where mainly the central transition is involved.

The results of a ^{11}B{^{29}Si} REDOR experiment, monitoring the second coordination sphere of a central boron atom, are presented as filled circles in Figure 4. The REDOR curve shows a quadratic dependence at short evolution times and a leveling off near $\Delta S/S_0 = 1$.

While the REAPDOR and REDOR experiments explore the heteronuclear intermediate-range ordering in the nitridic ceramic $Si_3B_3N_7$, ^{29}Si (and ^{11}B) static spin–echo decay spectroscopy experiments can be used to study homonuclear ordering phenomena on intermediate-distance scales. This approach has been shown to work for spin $^1/_2$ nuclei[24] as well as for noninteger quadrupolar nuclei.[25] The spin–echo decay at short evolution times can usually be described by a Gaussian according to $I/I_0 = \exp(-(2\tau)^2M_2/2)$.[25] M_2 denotes the second moment, given by the well-known van Vleck equation $M_2 = P(\mu_0/4\pi)^2\gamma^4I(I + 1)\hbar^2\sum r_{ij}{}^{-6}$,[26] where γ, I and r_{ij} are the gyromagnetic ratio, the spin quantum number, and the internuclear distance, respectively. The prefactor P can adopt values between $^4/_{15}$ (inhomogeneous case, quenching of the flip-flop term in the dipolar Hamiltonian) and $^3/_5$ (homogeneous case). Due to the $1/r^6$ dependence the contribution of the second coordination sphere usually amounts to 90–95% of the total second moment. Therefore, an estimation of the second moment M_2 principally allows for a calculation of the number of (homonuclear) second-nearest neighbors, thus being a further independent source of information with respect to the intermediate-range ordering motif in these ceramics. Figure 5a presents the normalized ^{29}Si spin–echo intensity as a function of the evolution time 2τ obtained in a static ^{29}Si spin–echo experiment; Figure 5b summarizes the ^{11}B static spin–echo data for $^{29}Si_3B_3N_7$ together with data for the reference compound h-BN.

Discussion

The presented data enable us to discuss the ordering phenomena in the nitridic ceramic $Si_3B_3N_7$ up to intermediate-distance scales. The short-range order in these materials is characterized by the presence of tetrahedral SiN_4 units and trigonally planar BN_3 polyhedra as the building units of the $Si_3B_3N_7$ network, as has been confirmed by ^{11}B line shape analysis and comparison to crystalline model compounds.[27–29]

While this short-range ordering motif in related nitridic ceramics has been demonstrated using different experimental approaches (vide supra), information about the structural organization of the network forming polyhedra SiN_4 and BN_3 on an intermediate-distance

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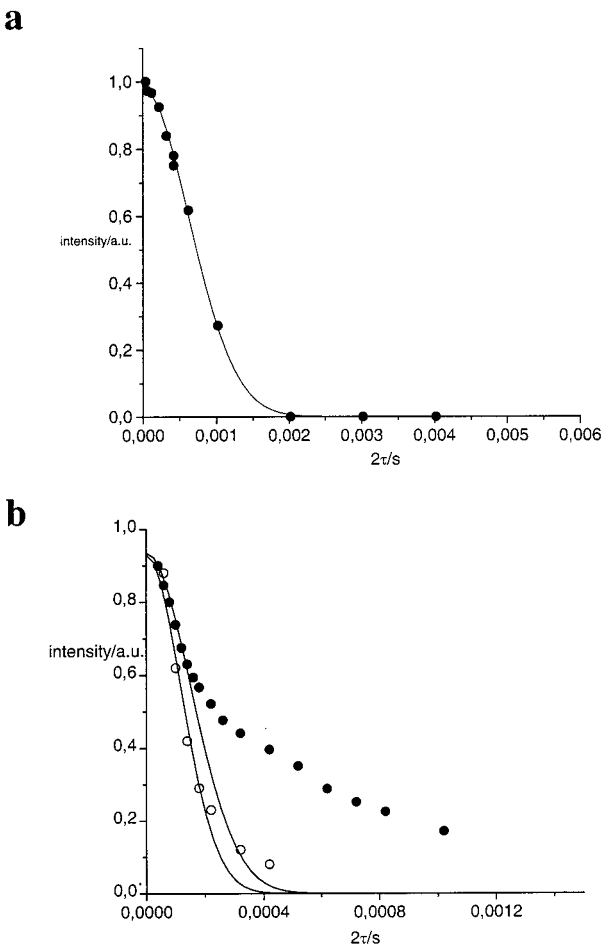

Figure 5. (a) ^{29}Si static dipolar spin−echo data (filled circles). The solid line corresponds to a fit resulting in $M_2 = 3.1 \times 10^6$ rad^2 s^{-2}. (b) ^{11}B static dipolar spin−echo data for $^{29}Si_3B_3N_7$ (filled circles) and h-BN (open circles). Solid lines correspond to M_2 values obtained by fitting the initial part of the decay curves ($2\tau < 200$ μs).

scale is only available on the basis of the presented REDOR and REAPDOR results. These experiments track the dipolar coupling strength between ^{11}B and ^{29}Si, hence principally supplying the number and distance of heteronuclei in the second coordination sphere.

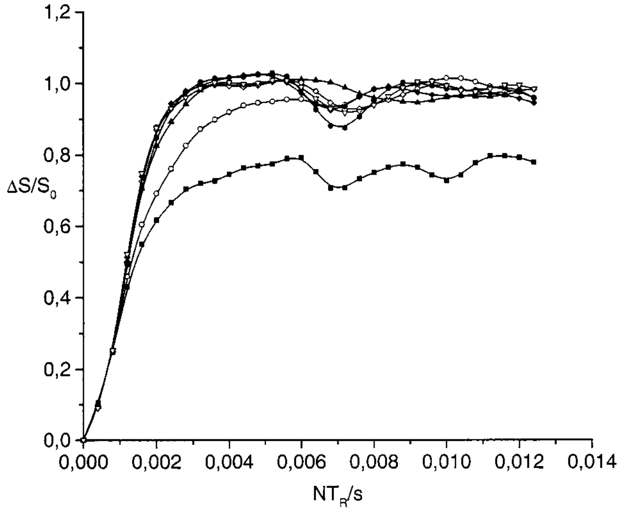

Figure 6. Compilation of calculated REAPDOR dephasing curves for a SiB$_2$ three-spin system. A distance B−Si of 2.74 Å was assumed. The angle spanned by the two dipolar vectors was varied from 20 to 180°. Key: open circles, 20°; filled triangles, 40°; open diamonds, 60°; filled circles, 80°; filled diamonds, 100°; open triangles, 120°; filled squares, 180°.

An analysis of the REAPDOR and REDOR curves has to account for multiple spin interactions.[30−32] Trigonally planar coordinated boron can be connected (via nitrogen) to up to six silicon atoms, while silicon may be coordinated to up to eight boron atoms in the second coordination sphere. Distribution of bond lengths and angles in amorphous networks further complicate interpretation of the data in smearing out the characteristic oscillations of the REAPDOR and REDOR curves at longer evolution times. Due to the low dephasing efficiency in the ^{29}Si{^{11}B} REDOR experiment we restrict the discussion to the ^{29}Si{^{11}B} REAPDOR and ^{11}B{^{29}Si} REDOR data. Analysis of the double resonance data was performed using self-written computer code, following the work of Naito et al.[30] and Chan et al. (REDOR)[31] and the simulation package SIMPSON.[33] Prior to the analysis of the presented data we performed numerous simulations of REDOR and REAPDOR curves, varying geometry and distribution for a given multiple spin interaction. Figure 6 contains a compilation of calculated REAPDOR curves for a BSi$_2$ three-spin system, varying the angle between the two dipolar vectors. We found that the initial parts of the REAPDOR and REDOR curves (in our case up to $\Delta S/S_0 = 0.5{-}0.6$) are fairly independent of the exact angle in a given geometry (see Figure 6) and distribution effects. Consequently, the obtained REDOR and REAPDOR curves can be analyzed in terms of number and distance of heteronuclei even if the exact geometry is unknown, provided the analysis is restricted to short evolution times. The simulation of the REAPDOR curves (Figure 7) was performed by assuming an internuclear distance Si−B of 2.74 Å, a value which is suggested by evaluation of neutron diffraction data.[8] Taking the natural abundance of the ^{11}B isotope (80.4%) into account, a single ^{29}Si−^{11}B dipolar coupling corresponding to a distance of 2.74 Å (380 Hz) produces the dashed lines, plotted in Figure 7a,b. Simulation of a three-spin interaction ^{29}Si−$^{11}B_2$ with the two internuclear ^{29}Si−^{11}B vectors spanning an angle α of 54° (corresponding to a trigonal planar NSiB$_2$ fragment), again assuming an internuclear distance of 2.74 Å, yields REAPDOR curves presented as dotted lines in Figure 7a,b. The experimental data can be simulated by a weighted superposition of both, according to 1.8 ± 0.1 boron neighbors in the second coordination sphere of a central silicon atom. In this calculation, the natural abundance of the ^{11}B isotope has been taken into account. Assuming 80% of silicon connected to two boron atoms and 20% of silicon connected to only one boron, this leads to $0.8 \times 0.8 \times 0.8 = 0.512$ as the fraction of silicon atoms which are connected to two ^{11}B nuclei ($0.8 \times 0.8 = 0.64$ is the probability that both neighbors are ^{11}B isotopes; the

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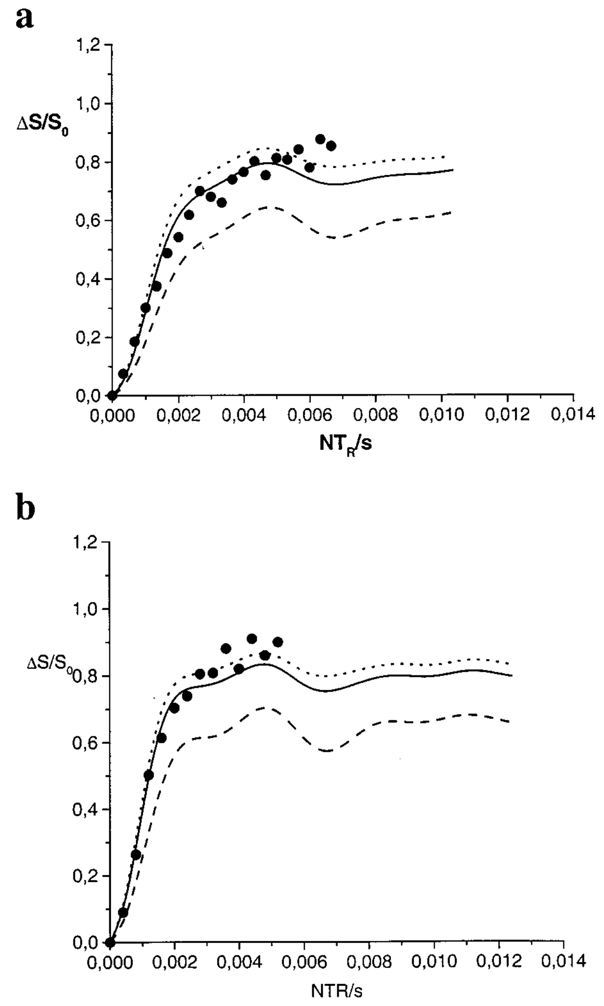

Figure 7. Simulation of the ^{29}Si{^{11}B} REAPDOR curves: (a) $\nu_{\mathrm{MAS}} = 5$ kHz, $\nu_{\mathrm{RF}}(^{11}\mathrm{B}) = 89$ kHz; (b) $\nu_{\mathrm{MAS}} = 6$ kHz, $\nu_{\mathrm{RF}}(^{11}\mathrm{B}) = 48$ kHz. Dashed lines: REAPDOR dephasing calculated for a single ^{29}Si$-^{11}$B dipolar coupling. Solid lines: REAPDOR dephasing curves calculated for a SiB_2 three-spin system with $\alpha = 54°$. Note that the dephasing curve for the SiB_2 three-spin system is actually a superposition of the dephasing curves for a two-spin and a three-spin interaction due to the natural abundance of the ^{11}B isotope (80.4%).

third 0.8 is the fraction of silicon connected to two boron atoms). In a similar vein, $0.8 \times 0.2 \times 0.8 + 0.2 \times 0.8 \times 0.8 = 0.256$ is the fraction of silicon atoms which are connected to two boron atoms but only connected to one ^{11}B nucleus. Correspondingly, an average number of 1.8 boron neighbors per silicon site would produce a REAPDOR curve according to $\Delta S/S_0^{\mathrm{total}} = 0.512(\Delta S/S_0^{\mathrm{threespin}}) + 0.416(\Delta S/S_0^{\mathrm{twospin}})$. While these simulations do not categorically exclude any contributions from higher spin systems (SiB_3, SiB_4, ...), they do indicate that the majority of silicon atoms is coordinated via nitrogen atoms to two boron sites. This implies that the network in the studied $Si_3B_3N_7$ ceramic is far from being homogeneous on an atomic level on the studied intermediate distance scale. Such a scenario would imply a mean number of four boron atoms in the second coordination sphere of silicon.

While the ^{29}Si{^{11}B} REAPDOR experiments elucidated the number and species of next nearest-neighbors of silicon, the reverse experiment, ^{11}B{^{29}Si} REDOR, monitors the second coordination sphere around a central boron atom. Analysis of the resulting REDOR curve was performed using the standard equation for REDOR dephasing[34] and adopting the approach of Naito[30] for multiple spin interactions. A weighted superposition of a two-spin and a three-spin interaction (with an angle $\alpha = 66°$ between the two dipolar vectors) succeeds in simulating the experimental data, resulting in 1.4 ± 0.1 silicon atoms in a distance of 2.74 Å per boron atom (Figure 8). Again a connectivity motif, characterized by preferred Si$-$N$-$Si and B$-$N$-$B linkages, emerges, leading to a network consisting of regions with predominantly B$-$N$-$B and regions with predominantly Si$-$N$-$Si bonding.

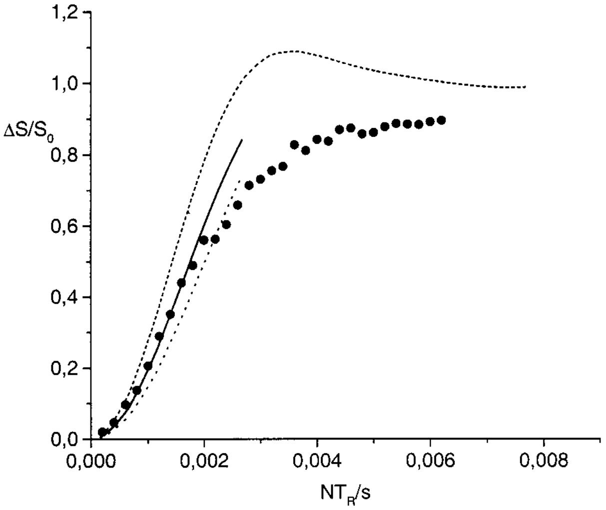

Figure 8. Experimental ^{11}B{^{29}Si} REDOR data together with simulated REDOR dephasing curves under the assumption of (a) one single B$-$Si dipolar coupling, $d = 2.74$ Å (dotted line), (b) two B$-$Si dipolar couplings, $d = 2.74$ Å (three-spin system BSi_2; $\alpha = 66°$ (dashed line)), and (c) weighted superposition of (a) and (b) according to $\Delta S/S_0 = 0.44\Delta S/S_0\,(BSi_2) + 0.56\Delta S/S_0\,(BSi)$.

The results of the ^{29}Si{^{11}B} REAPDOR experiments (1.8 boron atoms in the second coordination sphere of a central silicon) and the value of 1.4 silicon atoms in the second coordination sphere of a boron site found in the ^{11}B{^{29}Si} REDOR experiment perfectly support one another, considering the different coordination numbers of silicon and boron, resulting in a maximum possible number of atoms in the second coordination sphere of 6 and 8 for boron and silicon, respectively.

Even further support for our findings can be obtained when analyzing the dipolar static spin$-$echo behavior for ^{11}B and ^{29}Si. The experimental spin$-$echo decay of the ^{29}Si resonance in $Si_3B_3N_7$ is plotted in Figure 5a. The solid line corresponds to a M_2 of 3.1×10^6 rad^2 s^{-2}. This value can be related to the number of silicon atoms in the second coordination sphere of a central silicon atom as follows. A single ^{29}Si in a distance of 2.98 Å (concluded from neutron diffraction data[8]) contributes $(0.26-0.56) \times 10^6$ rad^2 s^{-2} to the second moment, depending on the value of the prefactor P. Although an a priori estimation of the prefactor is not possible, the value should be close to that for the homogeneous case, considering the narrow line width of the static ^{29}Si

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spectrum. With this assumption the number of silicon neighbors around a silicon site amounts to a (minimum) value of 6. This agrees well with the results of the REAPDOR experiments. Both approaches reveal 1.8 boron atoms and six silicon atoms comprising the second coordination sphere of a central silicon atom.

Interpretation of the ^{11}B spin−echo decay (Figure 5b) is complicated by the presence of the large quadrupolar interaction for the ^{11}B nucleus.[25,35] Gee et al.[25] found that the decay curves can be used to extract second moments only if analysis is restricted to short evolution times and selective pulses are used. Even under these conditions second-order quadrupolar interaction may lead to a suppression of the flip-flop term in the dipolar Hamiltonian and consequently to a drastic reduction of the second moment. We therefore compare the second moment M_2, found for the ceramic $Si_3B_3N_7$, to that of the model compound h-BN. In h-BN,[36] we find six boron atoms (in plane) at a distance of 2.51 Å, and six further boron atoms (three in the upper, three in the lower layer) at a distance of 3.61 Å, resulting in a $\sum r^{-6}$ value of 2.7×10^{58} m^{-6}. Since the quadrupolar line shape in h-BN is essentially identical to that of the ^{11}B signal in $Si_3B_3N_7$, we can assume the prefactor in the second moment to be identical for both compounds. The experimental second moment for the ^{11}B resonance in $Si_3B_3N_7$, obtained under various experimental conditions (nonselective and selective pulses), was in all cases determined to be 60−65% of the corresponding M_2(h-BN) value, leading to a value of 1.8×10^{58} m^{-6} for the $\sum r^{-6}$ part of the second moment. Assuming a B−B distance of 2.51 Å,[8] the contribution of a single boron atom amounts to 4×10^{57} m^{-6}, corresponding to 4−5 boron atoms in the second coordination sphere of a central boron atom. Together with the 1.4 silicon atoms these 4−5 boron atoms comprise the second coordination sphere of a central boron atom.

We are now in a position to present a structural model for the nitridic ceramics. All the presented results, ^{29}Si{^{11}B} REAPDOR, ^{11}B{^{29}Si} REDOR, and ^{11}B and ^{29}Si dipolar spin−echo spectroscopy, are consistent with the following network description.

The short-range order is characterized by SiN_4 and BN_3 polyhedra, which are the building blocks of the network. The ordering motif on an intermediate length scale (2−6 Å) is characterized by formation of Si−N-rich and B−N-rich regions, respectively. A representation of the resulting network is sketched in Figure 9, which illustrates the avoidance of Si−N−B connections, resulting in the formation of boron-rich and silicon-rich islands. This structural motif can be explained with the help of the kinetics of the ammonolysis of the $-BCl_2$ and $-SiCl_3$ groups in the precursor molecule TADB. The higher Lewis acidity of the BCl_2 fragment implies a faster attack of ammonia at the boron site of TADB. As a consequence, at the beginning of the reaction, only $-B-NH_2$ groups are available for the polycondensation. This in turn leads to an oligomer, which is predominantly characterized by B−N−B linkages. Si−Cl bonds are not attacked by ammonia unless the local B−Cl supply is almost depleted. The single B−N−Si linkage, already present in the precursor molecule, seems to survive the condensation and pyrolysis process, while the new linkages seem to be primarily B−N−B and Si−N−Si connectivities.

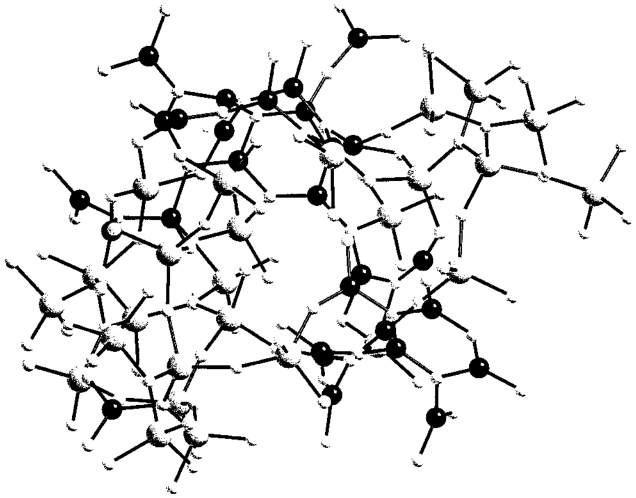

Figure 9. Proposed structural model for the $Si_3B_3N_7$ ceramic. The agglomeration of B−N−B and Si−N−Si units into boron- and silicon-rich regions, respectively, can be clearly drawn from this representation.

Conclusions

^{29}Si{^{11}B} REAPDOR and ^{11}B{^{29}Si} REDOR experiments on a 100% ^{29}Si isotopically enriched sample of the nitridic ceramic $Si_3B_3N_7$ were performed with the aim of elucidating the structural organization in the amorphous network on an intermediate length scale. Analysis of the resulting REDOR and REAPDOR curves involved multiple spin interactions. The results could be consistently explained assuming a network which is characterized by an agglomeration of B−N−B linkages and Si−N−Si linkages to form boron-rich and silicon-rich regions. Additional ^{11}B and ^{29}Si dipolar spin−echo decay experiments support these results.

The proposed network, concluded from the double resonance NMR data presented in this work, is consistent with the homogeneous elemental distribution on a length scale > 9 Å found by Heinemann et al.,[9] since the diameter of the proposed islands is in the range of 4−6 Å. Work to the end of extending these experiments to the quaternary ceramic $SiBN_3C$ is currently in progress in our laboratory.

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