Boron-modified perhydropolysilazane towards facile synthesis of amorphous SiBN ceramic with excellent thermal stability

Ying ZHAN\textsuperscript{a,†}, Wei LI\textsuperscript{a,†}, Tianshu JIANG\textsuperscript{a}, Claudia FASEL\textsuperscript{a}, Emmanuel III RICOHERMOSO\textsuperscript{a}, Jan BERNAUER\textsuperscript{a}, Zhaoju YU\textsuperscript{b,*}, Zhenghao WU\textsuperscript{c,*}, Florian MÜLLER-PLATHE\textsuperscript{c}, Leopoldo MOLINA-LUNA\textsuperscript{a}, Ralf GROTTE MNÜLLER\textsuperscript{d}, Ralf RIEDEL\textsuperscript{a}

\textsuperscript{a}Department of Materials and Earth Sciences, Technical University of Darmstadt, D-64287 Darmstadt, Germany
\textsuperscript{b}College of Materials, Key Laboratory of High Performance Ceramic Fibers (Xiamen University), Ministry of Education, Xiamen 361005, China
\textsuperscript{c}Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technical University of Darmstadt, D-64287 Darmstadt, Germany
\textsuperscript{d}Merck KGaA, Performance Materials, D-64293, Darmstadt, Germany

Received: November 14, 2021; Revised: April 1, 2022; Accepted: April 3, 2022
© The Author(s) 2022.

Abstract: SiBN ceramics are widely considered to be the most promising material for microwave-transparent applications in harsh environments owing to its excellent thermal stability and low dielectric constant. This work focuses on the synthesis and ceramization of single-source precursors for the preparation of SiBN ceramics as well as the investigation of the corresponding microstructural evolution at high temperatures including molecular dynamic simulations. Carbon- and chlorine-free perhydropolysilazanes were reacted with borane dimethyl sulfide complex at different molar ratios to synthesize single-source precursors, which were subsequently pyrolyzed and annealed under N\textsubscript{2} atmosphere (without ammonolysis) to prepare SiBN ceramics at 1100, 1200, and 1300 °C with high ceramic yield in contrast to previously widely-used ammonolysis synthesis process. The obtained amorphous SiBN ceramics were shown to have remarkably improved thermal stability and oxidation resistance compared to amorphous silicon nitride. Particularly, the experimental results have been combined with molecular dynamics simulation to further study the amorphous structure of SiBN and the atomic-scale diffusion behavior of Si, B, and N at 1300 °C. Incorporation of boron into the Si–N network is found to suppress the crystallization of the formed amorphous silicon nitride and hence improves its thermal stability in N\textsubscript{2} atmosphere.

Keywords: polymer-derived ceramics (PDCs); SiBN; crystallization; molecular dynamics; oxidation resistance

† Ying Zhan and Wei Li contributed equally to this work.
* Corresponding authors.
E-mail: Z. Yu, zhaojuyu@xmu.edu.cn;
Z. Wu, z.wu@theo.chemie.tu-darmstadt.de
1 Introduction

Nitride ceramics, such as Si$_3$N$_4$ and BN, have been ever-increasingly applied in several key areas owing to their chemical stability, relatively high thermal conductivity, and outstanding oxidation resistance even under extremely harsh environments [1–7]. However, the intrinsic weakness of creep and thermal shock resistance limits their scope of application. To tackle these shortcomings, adjustments can be performed at the microscale by lowering the atomic diffusivity and reducing stress concentrations [8–13], which are achievable in materials with amorphous networks. It has been reported that in materials having three or more elements with different and specific coordination numbers, the formation of a crystalline phase can be sufficiently suppressed [1,14–17]. However, the adaptability of this concept to nitride materials is challenging. Due to their low self-diffusion coefficients, ternary nitrides are difficult to be prepared via solid-state synthesis routes. In this context, the polymer-derived ceramic (PDC) route proves itself to be a promising method for preparing multielement ceramic nanocomposites. As polymer precursors can be tailored at the molecular level, end products with tunable chemical composition and homogeneous element distribution can be consequently achieved [18–23].

In recent years, ternary ceramics composed of Si, B, and N have attracted widespread attention due to their advanced properties as compared to single-component ceramics of Si$_3$N$_4$ and BN. Particularly, SiBN ceramics and Si$_3$N$_4$/BN composites with low dielectric constant are considered to be the most promising microwave-transparent materials for use in microwave windows and radomes under harsh environments. Various studies have been reported regarding the synthesis of ternary SiBN ceramics via molecular and PDC routes [14,24–31]. However, most of the reported polymer precursors used to prepare SiBN ceramics inevitably contain a certain amount of carbon. In order to eliminate the influence of carbon, complex and expensive pyrolysis (e.g., pyrolysis under NH$_3$ atmosphere) and annealing (under N$_2$ atmosphere) processes have to be applied to synthesize carbon-free SiBN ceramics [14,24,26,27,32]. Not only that, chlorine-containing precursors were employed, in which the chlorine is difficult to be removed during pyrolysis. Moreover, most studies have focused on the modification of precursors and the polymer-to-ceramic transformation, exclusively, and there is limited research on amorphous SiBN ceramic and its thermal stability.

In this work, carbon- and chlorine-free single-source precursor (boron-modified perhydropolysilazane) derived amorphous SiBN ceramics with varying chemical compositions were successfully prepared under N$_2$ (without expensive ammonolysis process). Molecular structure and the possible reaction mechanisms of the polymer precursors, as well as the relationship between microstructural evolution and the early stage crystallization of SiBN ceramics were investigated. Besides, the influence of Si/B ratio in the SiBN ceramics on both high temperature stability and resistance to crystallization was assessed. In addition to the experimental techniques, molecular dynamics (MD) simulation is employed to shed light onto the molecular structure and the atomic-level diffusion behavior of amorphous silicon nitride and SiBN, which provides a rational explanation for the polymer-to-ceramic transformation of SiBN ceramics.

2 Materials and methods

2.1 Synthesis and pyrolysis of single-source precursors

All the chemical syntheses were carried out under an argon atmosphere using standard Schlenk technique except where otherwise stated. Commercially available perhydropolysilazane solution (20 wt% of PHPS in dibutyl ether, Merck, KGaA, Germany) and borane dimethyl sulfide complex (BMS, Sigma-Aldrich, Germany) were used to synthesize the single-source precursors for the preparation of SiBN ceramics. To investigate the effect of boron content on phase composition, microstructural evolution, and oxidation resistance of the obtained SiBN ceramics, the Si/B molar ratios of the precursors were set to be 1, 2, and 5, according to the amount of BMS added to the PHPS solution. The synthesized boron-modified perhydropolysilazanes are denoted as BPSZ$X$ ($X$ is the set Si/B molar ratio) accordingly. Here, a representative synthesis process of the BPSZ2 is stated as follows: a solution of BMS (2.4 mL, 25 mmol) in anhydrous toluene (5 mL) was added dropwise to a solution of PHPS (11.25 g, 50 mmol, based on one monomer unit) with stirring at $\sim$ 78 °C (dry ice/acetone bath) for 2 h and naturally warmed up to room temperature. After stirring for 24 h continuously, the mixture was heated up to 80 °C for
3 h followed by vacuum drying at 50 °C to yield a milky white gel-like solid precursor. The dried solid single-source precursor was subsequently transferred into Schlenk tube furnace under the protection of argon and heated to 1100 °C for 2 h at a heating rate of 50 °C/h under a constant flow of N₂. The as-pyrolyzed specimen was annealed at 1200 and 1300 °C for 2 h in N₂ atmosphere to investigate their high-temperature crystallization behavior and stability against thermal decomposition.

2.2 Characterizations

The synthesis and the crosslinking process of the single-source precursors were analyzed ex situ by Fourier transform infrared (FTIR) spectroscopy on a Varian IR-670 spectrometer (Agilent Technologies, USA), using attenuated total reflection (ATR) mode in the range of 550–4000 cm⁻¹. Background corrections and baseline corrections of the spectra have been done automatically by the device. The quantitative elemental analyses of the synthesized precursor (BPSZ2) and BPSZ2-derived ceramic (pyrolyzed at 1100 °C) were performed at Mikroanalytisches Labor Pascher (Remagen, Germany). Silicon and boron contents were measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Hydrogen content was determined by combustion in pure oxygen and the detection of water using infrared spectroscopic. Nitrogen and oxygen contents in ceramic samples were detected by thermal conductivity and IR-analysis, respectively. Nitrogen and oxygen contents in polymeric sample were detected volumetrically and by thermal conductivity detection, respectively. Carbon analysis of samples annealed at 1300 °C was carried out by an LECO C-200 analyzer (LECO Corporation, St. Joseph, Michigan, USA). The phase compositions of the ceramic samples were investigated by X-ray diffraction (XRD) with a STADIP powder diffractometer (STOE & Cie GmbH, Germany, Mo Kα1 radiation source). To investigate the microstructure of the as-obtained ceramics, transmission electron microscopy (TEM) experiments were performed on an atomic resolution microscope (ARM) Jeol JEM-200F (JEOL Ltd, Tokyo, Japan) under electron beam energy of 200 keV. The high-resolution TEM images were filtered using an average background subtraction filter or a Wiener filter [33]. In parallel, scanning electron microscopy (SEM) was employed with a Philips XL30 FEG high-resolution scanning electron microscope (FEI Company, Hillsboro, Oregon, USA), coupled with an energy-dispersive X-ray (EDX) spectroscopy (Mahwah, New Jersey, USA). The polymer-to-ceramic transformation of the different precursors was characterized by means of thermogravimetric analysis/differential thermal analysis (TGA/DTA) in flowing nitrogen atmosphere with an STA 449C Jupiter (Netzsch Gerätebau GmbH, Germany) in situ coupled with a mass spectrometer (MS, QMS 403C Aëolos, Netzsch Gerätebau GmbH, Germany). The heating rate was set at 5 °C/min. TGA was employed as well to investigate the oxidation behavior of SiBN ceramic powders by observing their weight change from room temperature to 1350 °C with a heating rate of 5 °C/min in synthetic air.

2.3 Molecular dynamics simulation

Molecular dynamics simulations of amorphous silicon nitride and SiBN ceramics have been conducted using the large-scale atomic/molecular massively parallel simulator (LAMMPS) [34]. Many-body Tersoff potentials [35] were employed to describe the interactions among Si, B, and N. Structural properties, e.g., coordination number and pair distribution functions, of amorphous silicon nitride and SiBN materials simulated using this Tersoff potential have been demonstrated to be reasonably reproduced compared with experimental measurements [36]. Four amorphous ceramics systems, namely Si₃N₄, Si₃BₓN₄₋ₓ, Si₃B₁.₅N₅, and Si₃B₂N₇, have been simulated to study the influence of the boron content on the thermal stability of the amorphous ceramics at temperature T = 1300 °C, similar to the experiments. Initially, around 10,000 atoms were randomly placed in the simulation box at a density of ~2.5 g/cm³ (consistent with the experimental measurement for the bulk material at ~1500 K [37]) for all systems, giving a cubic dimension of ~5 nm. Details of the simulated systems can be found in the Electronic Supplementary Material (ESM). Subsequently, the system was pre-equilibrated for 20 ps at T = 8000 K to eliminate the impact of the initial atomic arrangement and to avoid its trapping in local energy minima. A fast quench under constant volume to T = 1300 °C followed. The quenched system was then subjected to an additional equilibration of 100 ps. The equilibration of the simulation was monitored via tracking its total potential energy. After about 20 ps, the potential energy reaches a plateau as seen in an example of Si₃B₂N₇ given in the ESM. After equilibration, the simulation was continued as production run (~5000 ps) for the
The structural properties of amorphous Si₃N₄, Si₃B₀.₆N₄.₆, Si₃B₁.₅N₅.₅, and Si₃B₃N₇ have been characterized via pair distribution functions, defined as

\[ g_{ij}(r) = \frac{V}{N_i N_j} \frac{dN_j(r)}{4\pi r^2 dr} \]  

where \( V \) is the volume of the simulation box. \( N_i \) and \( N_j \) denote the number of atoms of elements \( i \) and \( j \), respectively. \( \delta N_j(r) \) represents the number of atoms of element \( j \) within a shell of thickness \( dr \) at the distance of \( r \). The coordination number of element \( j \) around element \( i \) can then be calculated by

\[ Z_{ij} = \rho_j \int_0^{r_c} 4\pi r^2 g_{ij}(r)dr \]  

where \( r_c \) is the position of the first minimum in the pair distribution function between elements \( i \) and \( j \). \( \rho_j \) is the average number density of element \( j \).

The atomic dynamics have been measured via the mean-square-displacement (MSD), given by

\[ \text{MSD}(t) = \langle (r(t) - r(0))^2 \rangle \]  

where \( \langle \cdot \rangle \) denotes the ensemble average and \( r(t) \) is the atomic position vector at time \( t \). The diffusion coefficient has been derived by the Einstein relation:

\[ D = \frac{1}{6} \frac{d\text{MSD}(t)}{dt} \]  

3 Results and discussion

3.1 Synthesis of the single-source precursors

A set of boron-modified perhydropolysilazanes with different Si/B molar ratios were synthesized under Ar atmosphere and investigated with FTIR spectroscopy. The FTIR spectra of BMS, dried PHPS, and the obtained BPSZX precursors are shown and compared in Fig. 1. Typical absorption bands of N–H (1120 and 3302 cm⁻¹), Si–H (2159 cm⁻¹), and Si–N–Si (830–1050 cm⁻¹) groups are expectedly shown in the FTIR spectrum of PHPS. With the addition of BMS into PHPS, the N–H and Si–H groups of PHPS and the B–H (2391 cm⁻¹, stretching vibration) groups of BMS are consumed, while B–N groups (1315 cm⁻¹) are formed simultaneously, as shown in the spectra of BPSZX precursors. Hence, dehydrocoupling reactions between the N–H (Si–H) and B–H groups are proposed as reaction mechanisms and are shown schematically in Fig. 2 [40,41]. Unlike the N–H groups, which are reacted in a high amount, only a small number of the Si–H groups are involved in the modification process. It was reported by Hapke and Ziegler [42] that the reaction of Si–H groups is affected by steric hindrance during the chemical modification of the PHPS. Additionally, the existence of B–H (1091 cm⁻¹) groups in BPSZ1 and BPSZ2 reveals that the silazane-bonded B–H groups have not been completely reacted. The C–H vibrations (2786–2995 cm⁻¹) detected in the spectra of the BPSZX samples stem from the residual solvent dibutyl ether.

The elemental analyses of precursor BPSZ2 (Table 1) confirm the presence of boron atoms, indicating the successful incorporation of boron into the PHPS network. The empirical Si/B molar ratio (5.49) is larger than the set value (2), indicating boron loss during the


Table 1  Elemental composition of BPSZ2 precursor and BPSZ2-derived ceramic (pyrolyzed at 1100 ℃)

| Sample                  | Composition (wt%) | Calculated Si/B ratio | Empirical formula               |
|-------------------------|-------------------|-----------------------|---------------------------------|
| BPSZ2                   | 55.80 3.99 24.00 5.07 3.90 6.49 | 5.49                  | $\text{Si}_{1.00}\text{B}_{0.18}\text{N}_{0.86}(\text{C}_{0.16}\text{O}_{0.21}\text{H}_{0.55})$ |
| BPSZ2-derived ceramic   | 68.50 2.56 23.00 0.84 3.36 1.36 | 10.51                 | $\text{Si}_{1.00}\text{B}_{0.10}\text{N}_{0.67}(\text{C}_{0.11}\text{O}_{0.04}\text{H}_{0.34})$ |

synthesis process. The loss of boron is discussed in terms of (i) the evaporation of BMS during the synthesis and drying process and (ii) borane did not react with PHPS stoichiometrically due to steric hindrance imposed by the polymer structure, which is in good agreement with the observation of Viard et al. [40]. The found amounts of carbon and oxygen are attributed to the residual solvent dibutyl ether and the water contamination during the elemental analysis. The elemental content of the ceramics will be discussed in Section 3.2.

3.2 Polymer-to-ceramic conversion

The polymer-to-ceramic transformation and ceramic yield of the single-source precursors BPSZX were investigated via a combination of ex situ FTIR and in situ TGA/DTA measurements coupled with evolved gas analysis (EGA). As demonstrated in the TG curves (Fig. 3(a)), starting from room temperature to approximately 170 ℃, the dried PHPS shows a minor weight loss of 1 wt%, while the BPSZ5, BPSZ2, and BPSZ1 samples present obvious mass loss of 4, 3, and 8 wt%, respectively. Volatiles ($m/z = 27–72$) identified in the MS results (partly shown in Fig. 3(c) and Figs. S1(b) and S1(c) in the ESM) indicate that the mass loss of boron-modified BPSZX samples is due to the volatilization and decomposition of low-molecular-weight oligomers, especially silane and solvent (dibutyl ether).

In addition, the exothermic peak of BPSZ2 shown in Fig. 3(b) indicates proceeding dehydrocoupling reactions between Si–H (N–H) and B–H groups, with the release of H2 that has been detected with MS shown in Fig. 3(c). This assumption is further supported by the FTIR spectra of BPSZ2 shown in Fig. 4. The characteristic absorption bands of Si–H, N–H, and B–H groups decrease considerably, and the bands of C–H vibrations caused by the solvent disappear completely.

In the temperature range of 170–800 ℃, the dried PHPS shows a major weight loss of 22 wt%, where typical crosslinking reactions via dehydrocoupling and transamination take place, along with bond redistribution and thermal decomposition [43]. The weight loss is completed at ~800 ℃ with a ceramic yield of 77 wt%, which is in accordance with former reported data [44]. With the addition of boron, the weight loss of the precursor is significantly reduced from 23 wt% to at least 12 wt%. The second weight loss of BPSZX samples occurs between 170 and ~600 ℃. Similar to the dried PHPS, crosslinking of residual Si–H, N–H, and B–H groups takes place through dehydrocoupling reactions, which is confirmed by the continuous release of H2 detected by MS and supported by the corresponding ex situ FTIR spectra. However, due to the large consumption of N–H groups during the synthesis of the precursors, there is no obvious detection of NH3 in the TGA/EGA experiment, indicating that only few transamination reactions occur. Thanks to the

Fig. 3  (a) TG curves recorded for dried PHPS and BPSZX ($X = \text{Si/B}$ molar ratio) under N₂. (b) TG (dashed lines) and DTA (bold lines) curves of dried PHPS and BPSZ2 under N₂. (c) Ion current profiles (bold lines) of typical mass fragments during pyrolysis of BPSZ2 up to 1300 ℃ under N₂: hydrogen ($m/z = 2$), water ($m/z = 18, 19$), C₂H₃ ($m/z = 27$), SiH₄ ($m/z = 29, 30, 32$), amines ($m/z = 41, 43$, derivatives of Me₂NH), CO₂ ($m/z = 44$), C₄H₆ ($m/z = 56, 57$). Dashed line represents the corresponding TG curve.

www.springer.com/journal/40145
high crosslinking degree of BPSZX samples due to the incorporation of boron into PHPS, depolymerization and thermolysis at higher temperature are diminished. Therefore, a significantly increased ceramic yield is obtained with the boron-modified precursors.

Beyond 600 °C, the thermal behavior of the BPSZX samples with different Si/B molar ratio differs in the TGA measurements. The BPSZ2 sample exhibits the best thermal stability with a negligible mass loss and has a final ceramic yield of 92 wt% at 1300 °C, indicating that the polymer-to-ceramic transformation has been already accomplished at ~600 °C. The ceramization process is supported by the ex situ FTIR spectra (Fig. 4), where the absorption bands of Si–H and N–H almost completely vanish beyond 500 °C. On this account, further investigations focus more on the BPSZ2 sample. With less boron content, the BPSZ5 sample goes through a sudden mass loss (3 wt%) between 800 and 930 °C, which is attributed to the thermal decomposition of the preceramic polymer, as confirmed by the endothermic peak shown in the DTA curve (Fig. S1(a) in the ESM). Nevertheless, the ceramic yield of BPSZ5 is still higher than that of dried and pristine PHPS, and ends up as 88 wt% at 1300 °C. With more boron incorporation, the BPSZ1 sample gains 3 wt% of mass between 600 and 1300 °C, and has a final ceramic yield of ~91 wt%. The analyzed mass gain is ascribed to the reaction between residual boron and N2 [45,46]. Additionally, the dried PHPS shows a mass gain of 6 wt% at ~1250 °C due to the crystallization process of ZnO, which will be discussed in Section 3.3.

The chemical composition of the obtained BPSZ2-derived ceramic pyrolyzed at 1100 °C shown in Table 1 confirms the formation of SiBN ceramic. During the polymer-to-ceramic conversion, another fraction of boron is lost due to the further volatilization of borane species, resulting in a final Si/B molar ratio of 10.51. In addition, the elemental analysis of BPSZ-derived ceramics (Table 2) confirms the removal of carbon after annealing at 1300 °C. In summary, compared with the former reported ceramic yield (~55 wt% [27], 72 wt% [32]) of SiBN ceramics obtained via other synthesis methods, higher ceramic yield was achieved with the current method (88–92 wt%).

### 3.3 Crystallization and microstructural evolution of the as-prepared ceramics

The structural evolution and crystallization behavior of annealed PHPS and BPSZX samples have been investigated after heat treatment at various temperatures (1100, 1200, and 1300 °C) by XRD, TEM, and EDX spectroscopy. The XRD patterns of the PHPS- and BPSZX-derived ceramics obtained upon annealing at different temperatures are shown in Fig. 5. At 1100 °C, all the as-prepared ceramics are predominantly X-ray amorphous. At 1200 °C, the boron-free PHPS-derived specimen exhibits a low-intensity reflection of α-Si3N4, while all the BPSZX-derived ceramics remain X-ray amorphous. As the annealing temperature further increases to 1300 °C, crystallization of α-Si3N4 is induced in the annealed PHPS sample. According to the weight gain (6 wt%) presented in the TG curve and the exothermal peak shown in the DTA curve (Fig. 3(b)), the crystallization temperature of PHPS-derived ceramic is suggested to be in the range of 1200–1300 °C [47]. In the meantime, as the boron content increases in the BPSZX samples, the emergence of α-Si3N4 is hindered. The crystallization of BPSZ5- and BPSZ2-derived ceramics gradually takes place at temperature up to 1300 °C, while the XRD pattern of the BPSZ1-derived ceramic is still X-ray amorphous. These results clearly demonstrate that the incorporation of boron into Si–N network suppresses the crystallization of Si3N4, which is attributed to the higher crystallization temperature of the formed ternary Si–B–N system, and which thereby restricts the crystallization of both Si3N4 and BN [15,48].

| Sample   | BPSZ1-derived ceramic (wt%) | BPSZ2-derived ceramic (wt%) | BPSZ5-derived ceramic (wt%) |
|----------|-----------------------------|-----------------------------|-----------------------------|
| Carbon content | 0.35 | 0.49 | 0.24 |
Fig. 5 XRD patterns of the as-pyrolyzed (a) PHPS and (b–d) BPSZ\(X\) (\(X = \text{Si/B molar ratio}\)) samples annealed at different temperatures. All samples annealed at 1100 °C are X-ray amorphous. The PHPS-derived ceramic starts to crystallize upon 1200 °C, while the boron-modified BPSZ\(X\) samples remain X-ray amorphous. Along with the increase of the boron content (from b to d), the crystallization of BPSZ\(X\) samples is suppressed.

The microstructure of the as-prepared PHPS and BPSZ2-derived ceramics annealed at 1300 °C were further investigated by TEM along with the selected area electron diffraction (SAED) pattern, SEM, and EDX spectroscopy. As shown in Fig. 6(a), the high-resolution TEM (HRTEM) image of the annealed PHPS-derived ceramic exhibits a typical nanocrystalline structure with a lattice spacing of 0.21 nm, which corresponds to the \(d\)-spacing of the (202) \(\alpha\)-Si\(_3\)N\(_4\) lattice plane (JPCDS Card No. 09-0250). Furthermore, the SAED pattern (inset in Fig. 6(a)) presents diffraction spots of \(\alpha\)-Si\(_3\)N\(_4\) crystals, which agrees with the XRD results (Fig. 5).

As revealed by Fig. 6(b), both the TEM image and the SAED pattern affirm that the as-prepared BPSZ2-derived ceramic remains amorphous, which is consistent with the results obtained from the XRD as well. The SEM micrograph (Fig. 7(a)) of BPSZ2-derived ceramic annealed at 1300 °C shows a dense structure. As can be

Fig. 6 Filtered HRTEM images of (a) PHPS- and (b) BPSZ2-derived ceramics annealed at 1300 °C. Insets are the corresponding SAED patterns.
Fig. 7  SEM graph and elemental mappings of the BPSZ2-derived ceramic prepared with a Si/B ratio of 2:1 and annealed at 1300 °C, indicating a dense SiBN ceramic structure with homogeneous Si, B, and N elemental distributions.

seen from the corresponding elemental mapping (obtained from EDX) displayed in Figs. 7(b)–7(d), Si, B, and N elements are distributed homogenously in the amorphous structure with no obvious agglomeration being observed.

3.4 Molecular dynamics simulations

According to previous theoretical calculation studies [16,36,49], boron incorporation has a significant influence on the crosslinking and pyrolysis processes of Si–N networks. Short-range atomic arrangements are characterized by total and partial pair distribution functions (PDF) of amorphous Si₃N₄ and SiBN ceramics with different boron content. As shown in Figs. 8(a) and 8(b), all PDFs converge to a constant value of 1 for radii larger than 0.5 nm, indicating long-range amorphous disorder in the ceramics. As shown in Fig. 8(b), the first peak of SiBN ceramics at a distance of 0.149 nm is not only closer than that of any other pair, but also much higher. It corresponds to B–N distances and indicates the strong bonding between these elements. This characteristic distance is in good agreement with the range of B–N bond lengths obtained from experiments and density functional theory calculations

Fig. 8  (a) Total pair distribution functions for amorphous ceramics Si₃N₄ (black), SiₓB₀.6N₄.₆ (blue), SiₓB₁.₅N₅.₅ (purple), and SiₓB₃N₇ (red); (b) partial pair distribution functions calculated from SiₓN₄ (dashed lines) and SiₓBₓNₓ₋ₓ (solid lines) for Si–Si, Si–N, N–N, B–N, and Si–B pairs; (c) coordination numbers as a function of B/Si ratio for center atoms of Si (top) surrounded by N atoms and B atoms, and N (bottom) surrounded by Si atoms and B atoms.
Moreover, the height of this peak increases with boron content, suggesting that more boron atoms surrounding any given nitrogen atom. Sharp peaks at a distance of ~0.17 nm are seen in the total PDFs for all investigated ceramics, which are due to Si–N pairs in the partial PDFs. The Si–N bond length is found here to be roughly 0.17 nm, which is similar to the value estimated from experiments (0.173–0.175 nm) [52–54]. In addition, peak for Si–B pairs (~0.28 nm) has a much lower height than that for Si–N or B–N observed in the partial PDFs of SiBN ceramics, suggesting that the formation of Si–B bonds is disfavored.

From the PDFs, the coordination numbers have been calculated. In Fig. 8(c), the coordination numbers of central Si and N atoms are shown as a function of the B/Si atomic ratio. The coordination number of Si surrounded by B (Si–B) increases as the B/Si atomic ratio increases, which implies that the Si–B bonds are more likely to form when more boron atoms are added. In the meantime, the coordination number of Si(N) (Si–N) slightly decreases. On the other hand, the coordination number of N(Si) (N–Si) decreases rapidly as B/Si atomic ratio increases, while the coordination number of N(B) (N–B) increases, indicating that the boron incorporation influences more on the N atoms than Si atoms.

The atomic mobility was also investigated in amorphous silicon nitride and various SiBN ceramics. The obtained mean-square displacements (MSDs) of Si, N, and B atoms are shown in Figs. 9(a)–9(c), respectively. The MSDs of Si are similar in all investigated ceramics, indicating a minor influence of boron incorporation on the Si diffusivity. In contrast, the MSDs of N in all SiBN ceramics are lower than that in Si3N4, and they decrease further with increasing boron content. This suggests that the incorporation of boron into the Si–N network restricts the atomic motion of both boron and nitrogen in the Si–B–N systems because of the formation of B–N bonds. These B–N bonds are not only copious (cf. Fig. 8), but also strong, and the system stability is hence improved.

From the limiting slopes of MSD curves, the atomic self-diffusion coefficients have been evaluated using the Einstein relation (Eq. (4)) [55]. For each element, its slope has been obtained from a linear part of the respective MSD within the time period of 900–1100 ps. As shown in Fig. 9(d), the self-diffusion coefficient of silicon is basically unaffected by the boron concentration.

![Fig. 9 Mean-square displacement curves of (a) silicon, (b) nitrogen, and (c) boron atoms, and (d) corresponding atomic self-diffusion coefficients in SiBN ceramics with different elemental compositions at 1300 °C.](www.springer.com/journal/40145)
within the margin of error. In contrast, the atomic diffusion coefficients of nitrogen and boron decrease significantly with increasing boron content, consistent with the formation of B–N bonds as seen in the peaks of B–N pairs in the pair distribution functions (Fig. 8). This is due to the strong mutual attraction of B and N, which in the Tersoff potential is much stronger than Si–B and B–B interactions. Furthermore, the presence of B–N bonds prevents N atoms from diffusing in the Si–B–N network and plays the part of rigid linkages. This impedes the formation of crystallites even at high temperatures. Similar behaviors are also found in the relaxation properties such as Van-Hove correlation functions and intermediate scattering functions in the ceramics with different boron contents. Detailed discussion can be found in the ESM. In conclusion, the addition of boron enables the formation of rigid B–N bonds and consequently reduces the atomic diffusivity of nitrogen atom in the network, and therefore, the thermal stability of amorphous Si–B–N is considerably enhanced relative to amorphous Si–N.

3.5 Oxidation behavior

The BPSZ\textsubscript{X}-derived ceramics were annealed at 1300 °C and oxidized in air at a temperature up to 1350 °C. The oxidation resistance of the corresponding ceramics was studied by the TG curves shown in Fig. 10, in which the triangle markers represent the amorphous silicon nitride data extracted from the work of Ma et al. [56]. Starting from 30 to 1000 °C, the amorphous silicon nitride exhibits a significant weight gain of 25.7 wt%.

![Fig. 10 TG curves of the as-prepared BPSZ\textsubscript{X}-derived ceramics (annealed at 1300 °C) performed within a temperature range from ambient temperature to 1350 °C in air. TG data points of amorphous silicon nitride are extracted from the work of Ma et al. [56].](image)

It is well documented in the literature that large numbers of unsaturated Si–N and Si dangling bonds in amorphous silicon nitride, such as Si dangling bonds and N vacancies, lead to severe vacancy oxidation (nitrogen vacancies occupied by oxygen atoms) and replacement oxidation (nitrogen atoms being replaced by oxygen atoms) [56,57]. In contrast, amorphous BPSZ\textsubscript{5}-derived ceramic displays negligible weight gain of 0.8 wt%, and the BPSZ\textsubscript{2}-, and BPSZ\textsubscript{1}-derived ceramics present no weight change at the temperature of 1000 °C. Moreover, by oxidation at 1350 °C, the BPSZ\textsubscript{5}-, BPSZ\textsubscript{2}-, and BPSZ\textsubscript{1}-derived amorphous ceramics yield mass gains of 5.1, 2.1, and 2.4 wt%, respectively, indicating improved oxidation resistance if compared with amorphous silicon nitride. As aforementioned, the presence of B atoms in amorphous Si–N networks not only occupies part of the unsaturated spaces, but also promotes the formation of B–N rigid linkages, resulting in superior oxidation resistance compared to amorphous silicon nitride. The proposed oxidation mechanisms of SiBN ceramics are illustrated in Eqs. (5)–(10) [58,59], which are suggested to be responsible for the weight gains between 1000 and 1350 °C. Due to the formation of B\textsubscript{2}O\textsubscript{3} in the silica, boron silicate glass is formed, which limits the O\textsubscript{2} inward diffusion and further B\textsubscript{2}O\textsubscript{3} volatilization. Furthermore, as reported by former research studies [60,61], with the addition of boron, a dual surface layer of B–N–O/SiO\textsubscript{2} is formed during oxidation to protect the ceramic from further oxidation, and hence increases the oxidation resistance.

\[
\text{Si(s)} + \text{O}_2(g) \rightarrow \text{SiO}_2(s)
\]

\[
2\text{Si(s)} + \text{O}_2(g) \rightarrow 2\text{SiO}(g)
\]

\[
2\text{SiO}(g) + \text{O}_2(g) \rightarrow 2\text{SiO}_2(s)
\]

\[
4\text{B(s)} + 3\text{O}_2(g) \rightarrow 2\text{B}_2\text{O}_3(l)
\]

\[
2\text{N(s)} + \text{O}_2(g) \rightarrow 2\text{NO}(g)
\]

\[
\text{N(s)} + \text{O}_2(g) \rightarrow \text{NO}_2(g)
\]

4 Conclusions

In the present work, ternary SiBN ceramics with different Si/B molar ratios have been successfully prepared via the PDC route starting from carbon- and chlorine-free single-source precursors, synthesized by modifying perhydropolysilazane (PHPS) with borane dimethyl sulfide complex (BMS). It has been proved
that both Si–H and N–H bonds of the PHPS react with B–H bonds of BMS through dehydrocoupling reaction during the synthesis of the BPSZX precursors. The precursor-to-ceramic transformation was investigated systematically with respect to crosslinking and crystallization. The TGA and FTIR results reveal that incorporation of boron considerably improves the crystallizing degree of the preceramic polymer, and consequently, the ceramic yield increases from 77 wt% (PHPS) to 88–92 wt% (BPSZX) upon pyrolysis under N2 atmosphere. Besides, without employing the costly ammonia, our reported method proves itself to be a facile and economic method for the synthesis of SiBN ceramic with high ceramic yield as opposed to former reported ammonolysis synthesis process. Furthermore, the resultant BPSZX-derived ceramics are shown to possess remarkable resistance against crystallization in comparison to PHPS-derived boron-free Si3N4 ceramics. This characteristic is ascribed to the decreased self-diffusion coefficient of nitrogen in the ternary ceramic, due to the formation of rigid B–N bonds in the Si–B–N network. In conclusion, the boron modification of Si–N via the PDC route presents a significant effect on its high-temperature resistance behavior with respect to crystallization and oxidation, which is of great significance for the design and manufacture of ternary Si-based and/or boron-containing ceramics.

The influence of boron on the phase evolution, mechanical and functional properties of SiBN ceramics, such as Young’s modulus, hardness, high-temperature self-healing capability, thermal and electrical conductivities, as well as the related applications have not been clarified unambiguously so far, and will be investigated in future studies.

Acknowledgements

The authors would like to acknowledge Merck KGaA for the financial support of this research project. Wei Li acknowledges financial support from China Scholarship Council (No. 201907040060) during his research at TU Darmstadt. Zhenghao Wu acknowledges the funding of Deutsche Forschungsgemeinschaft via the SFB-TRR 146 “Multiscale Simulation Methods for Soft Matter Systems”, Project A8.

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Electronic Supplementary Material

Supplementary material is available in the online version of this article at https://doi.org/10.1007/s40145-022-0597-z.

References

[1] Riedel R, Kienzle A, Dressler W, et al. A silicoboron carbonitride ceramic stable to 2,000 °C. Nature 1996, 382: 796–798.
[2] Riley FL. Silicon nitride and related materials. J Am Ceram Soc 2000, 83: 245–265.
[3] Bocanegra-Bernal MH, Matovic B. Mechanical properties of silicon nitride-based ceramics and its use in structural applications at high temperatures. Mater Sci Eng A 2010, 527: 1314–1338.
[4] Ionescu E, Kleebe H-J, Riedel R. Silicon-containing polymer-derived ceramic nanocomposites (PDC-NCs): Preparative approaches and properties. Chem Soc Rev 2012, 41: 5032–5052.
[5] Eichler J, Lesniak C. Boron nitride (BN) and BN composites for high-temperature applications. J Eur Ceram Soc 2008, 28: 1105–1109.
[6] Zhou Y, Hyuga H, Kusano D, et al. Development of high-thermal-conductivity silicon nitride ceramics. J Asian Ceram Soc 2015, 3: 221–229.
[7] Colombo P, Mera G, Riedel R, et al. Polymer-derived ceramics: 40 years of research and innovation in advanced ceramics. J Am Ceram Soc 2010, 93: 1805–1837.
[8] Mukhopadhyay A, Basu B. Consolidation-microstructure-property relationships in bulk nanoceramics and ceramic nanocomposites: A review. Int Mater Rev 2007, 52: 257–288.
[9] Sommers A, Wang Q, Han X, et al. Ceramics and ceramic matrix composites for heat exchangers in advanced thermal systems—A review. Appl Therm Eng 2010, 30: 1277–1291.
[10] Wang H, Singh RN. Thermal shock behaviour of ceramics and ceramic composites. Int Mater Rev 1994, 39: 228–244.
[11] Riedel R, Ruswisch LM, An LN, et al. Amorphous silicoboron carbonitride ceramic with very high viscosity at temperatures above 1500 °C. J Am Ceram Soc 1998, 81: 3341–3344.
[12] Wang ZC, Aldinger F, Riedel R. Novel silicon-boron-carbon-nitrogen materials thermally stable up to 2200 °C. J Am Ceram Soc 2001, 84: 2179–2183.
[13] Wan JL, Duan RG, Gasch MJ, et al. Highly creep-resistant silicon nitride/silicon carbide nano-nano composites. J Am Ceram Soc 2006, 89: 274–280.
[14] Ge KK, Ye L, Han WJ, et al. Pyrolysis of polyborosilazane and its conversion into SiBN ceramic. Adv Appl Ceram 2014, 113: 367–371.
[15] Zhou C, Gao X, Xu Y, et al. Synthesis and high-temperature...
evolution of single-phase amorphous Si–Hf–N ceramics. J Adv Ceram 2015, 35: 2007–2015.

[16] Liao NB, Xue W, Zhang M. Molecular dynamics investigation of Si–B–N ceramics: Effects of boron content. Model Simul Mat Sci Eng 2012, 20: 035009.

[17] Yu ZJ, Yang YJ, Mao KW, et al. Single-source-precursor synthesis and phase evolution of SiC–TaC–C ceramic nanocomposites containing core–shell structured TaC@C nanoparticles. J Adv Ceram 2020, 9: 320–328.

[18] Wen QB, Xu YP, Xu BB, et al. Single-source-precursor synthesis of dense SiC/HfC$_N$$_{1−x}$-based ultrahigh-temperature ceramic nanocomposites. Nanoscale 2014, 6: 13678–13689.

[19] Ionescu E, Bernard S, Lucas R, et al. Polymer-derived ultra-high temperature ceramics (UHTCs) and related materials. Adv Eng Mater 2019, 21: 1900269.

[20] Liu XM, Yu ZJ, Ishikawa R, et al. Single-source-precursor derived RGO/CNTs–SiCN ceramic nanocomposite with ultra-high electromagnetic shielding effectiveness. Acta Mater 2013, 80: 112–120.

[21] Wen QB, Yu ZJ, Riedel R. The fate and role of in situ formed carbon in polymer-derived ceramics. Prog Mater Sci 2020, 109: 100623.

[22] Yu ZJ, Lv X, Lai SY, et al. ZrC–ZrB$_2$–SiC ceramic nanocomposites derived from a novel single-source precursor with high ceramic yield. J Adv Ceram 2018, 9: 617–628.

[23] Jin SY, Gao KK, Qi HM, et al. High yield polyborosilazane precursor for SiBN ceramics. Adv Funct Mater 2014, 1004–1005: 409–414.

[24] Li WH, Wang J, Xie ZF, et al. Preparation of hollow Si–B–N ceramic fibers by partial curing and pyrolysis of polyborosilazane fibers. Mater Lett 2012, 78: 1–3.

[25] Liu Y, Chen KZ, Dong FB, et al. Effects of hydrolysis of precursor on the structures and properties of polymer-derived SiBN ceramic fibers. Ceram Int 2018, 44: 10199–10203.

[26] Liu Y, Peng S, Cui YJ, et al. Fabrication and properties of precursor-derived SiBN ternary ceramic fibers. Mater Des 2017, 128: 150–156.

[27] Long X, Shao CW, Wang YD. Effects of boron content on the microwave-transparent property and high-temperature stability of continuous SiBN fibers. J Am Ceram Soc 2020, 103: 4436–4444.

[28] Baldus P, Jansen M, Sporn D. Ceramic fibers for matrix composites in high-temperature engine applications. Science 1999, 285: 699–703.

[29] Baldus H-P, Jansen M. Novel high-performance ceramics—Amorphous inorganic networks from molecular precursors. Angew Chem Int Ed Engl 1997, 36: 328–343.

[30] Baldus H-P, Wagner O, Jansen M. Synthesis of advanced ceramics in the systems Si–B–N and Si–B–N–C employing novel precursor compounds. MRS Proceedings 1992, 271: 821.
[51] Andriotis AN, Richter E, Menon M. Prediction of a new graphenelike Si$_2$BN solid. Phys Rev B 2016, 93: 081413.

[52] Aiyama T, Fukunaga T, Niihara K, et al. An X-ray diffraction study of the amorphous structure of chemically vapor-deposited silicon nitride. J Non Cryst Solids 1979, 33: 131–139.

[53] Ténégal F, Flank AM, Cauchetier M, et al. Nanometric Si/C/N powders: Description of the short range atomic structure by X-ray absorption spectroscopy. Nucl Instrum Methods Phys Res B 1997, 133: 77–83.

[54] M Hagenmayer R, Müller U, J Benmore C, et al. Structural studies on amorphous silicon boron nitride Si$_3$B$_3$N$_7$; Neutron contrast technique on nitrogen and high energy X-ray diffraction. J Mater Chem 1999, 9: 2865–2869.

[55] Einstein A. On the movement of small particles suspended in stationary liquids required by the molecular kinetic theory of heat. Ann Phys 1905, 17: 549–560.

[56] Ma DH, Wang HJ, Niu M, et al. Oxidation behavior of amorphous silicon nitride nanoparticles. Ceram Int 2018, 44: 1443–1447.

[57] Zhang LD, Mo CM, Wang T, et al. Structure and bond properties of compacted and heat-treated silicon nitride particles. phys stat sol (a) 1993, 136: 291–300.

[58] Li DX, Yang ZH, Jia DC, et al. High-temperature oxidation resistance of dense amorphous boron-rich SiBCN monoliths. Corros Sci 2019, 157: 312–323.

[59] Dai J, Zhang Y, Gao D, et al. Oxidation behavior of amorphous Si–(B)–C–N ceramic in ambient air. Rare Metal 2011, 30: 557–562.

[60] Braue W, Paul G, Baldus HP. Microstructural response of SiBN$_2$C-fibers upon annealing in oxidizing and reducing atmospheres. In: High Temperature Ceramic Matrix Composites. Krenkel W, Naslain R, Schneider H, Eds. Germany: Wiley-VCH, 2001: 96–98.

[61] Cinibulk MK, Parthasarathy TA. Characterization of oxidized polymer-derived SiBCN fibers. J Am Ceram Soc 2001, 84: 2197–2202.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.