Synthesis and characterization of a novel polyborosilazane for SiBNC ceramic

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Abstract. A novel polyborosilazane (PBSZ) for preparing SiBNC ceramics was successfully synthesized via co-condensation approach using tetrachlorosilane (SiCl₄), trichloride (BCl₃) and propylamine (C₃H₇NH₂) as starting materials. After pyrolysis of these precursors, amorphous SiBNC ceramics were obtained. The chemical composition, structure and thermal stability of the synthesized PBSZ precursor and SiBNC ceramics were analyzed by using FT-IR, NMR, TGA and XRD methods. The results indicated that the PBSZ contained the major framework of \(-\text{Si-N-B-}\) and six-membered boron-nitrogen rings. The PBSZ precursor had an approximately ceramic yield of 63 wt% pyrolyzed at 900°C in nitrogen atmosphere. The SiBNC ceramics shows excellent oxidation resistance and maintained amorphous up to 1600°C.

1. Introduction
Non-oxide amorphous ceramic derived from preceramic polymers have been researched in recent years, such as BN (derived from polycarbosilane), SiC (derived from polyborazine) and SiBNC (derived from polyborosilazane) [1-5]. Among them, the quaternary system SiBNC due to its fine chemical stability, low density, high temperature stability and excellent oxidation resistance, were appropriate for application in high temperature applications and have drawn much attentions [6,7]. However, it is difficult to prepare SiBNC ceramics using traditional powder sintering methods. Up to date, the most feasible approach to prepare SiBNC ceramic (fibers) is the polymer-derived ceramics (PDCs) route [8]. Therefore, to prepare high performance SiBNC ceramics, the key step is to prepare high performance polymer precursor (that is, polyborosilazane, PBSZ) [9-11].

With the aim of improving the performance of PBSZ, many researchers have synthesized many different kinds of PBSZ. For instance, Sneddon et al [12] prepared high-yield borazine-substituted hydridopolysilazanes via the reaction of liquid borazine with hydridopolysilazane (HPZ). The boron-modified polymers have higher ceramic yield than the unmodified hydridopolysilazane on account of the structures of borazine-boron in the ceramic. Bernard et al [13] prepared \([\text{B(C}_2\text{H}_4\text{SiCH}_3\text{NCH}_3]_3\) through the aminolysis of \([\text{B(C}_2\text{H}_4\text{SiCH}_3\text{Cl}_2]_3\) (tris(dichlorosilylethyl)boranes). Jansen et al [14] synthesized precursors by cross-linking of \(\text{Cl}_3\text{Si-CH}_2\text{-BCl}_2\) (trichlorosilyl dichloroboryl methane), \((\text{CH}_3)\text{Cl}_3\text{Si-CH}_2\text{-BCl}_2\) (dichlorosilyl dichloroboryl methane) and methylamine. The obtained SiBNC ceramic have high-temperature stability and remarkable high-temperature oxidation resistance in air atmosphere at least up to 1300°C. However, Most synthesis routes are multiple-step, which adding complexity to the process and producing by-product [15,16]. Moreover, both molecular and
intermediates are sensitive to moisture, the whole reaction process should keep in sufficiently inert and dry environment and it is difficult to multiple-step processes [17,18].

In this paper, a novel PBSZ was prepared via a copolymerization of BCl$_3$, SiCl$_4$ and C$_3$H$_7$NH$_2$. Moreover, the structure and performance of the obtained PBSZ were studied.

2. Experimental procedures

2.1. Materials
BCl$_3$ solved in n-hexane were provided by Beijing Multi-Technology Co. n-hexane were provided by Sinopharm Chemical Reagent Co. Ltd. SiCl$_4$ with 99.99% purity were purchased from Bai Lingwei Chemical Co. C$_3$H$_7$NH$_2$ with 98.50% purity were obtained from Guoyao Chemical Co. Ltd. Nitrogen with 99.99% purity were used during preparation.

2.2. Polymer precursor synthesis
The glass reaction vessels were dried for 4 h at 100$^\circ$C. Then vacuumed and filled with high purity nitrogen (N$_2$). Dried n-hexane (3 L) was cooled to -15 ~ -20$^\circ$C, and then C$_3$H$_7$NH$_2$ (600 ml) dissolved in the pre-dried n-hexane. The mixture of BCl$_3$ (440 ml) and SiCl$_4$ (50 ml) dissolved in 440 ml n-hexane was gradually added into the mixture solution of C$_3$H$_7$NH$_2$ and n-hexane with fully mechanical stirring (the temperature $\leq$ -15$^\circ$C). Then the solution was stirred overnight at room temperature. After the solution standing for an hour, the upper clear liquid was collected and the byproduct was filtered. As a result, about 300 ml oligomers of polyborosilizane could obtained. The oligomers was polymerized at 180-230$^\circ$C for 50-60 h to gain PBSZ with appropriate viscosity.

2.3. Polymer to ceramic conversion
The obtained PBSZ has lots of active groups, so it was extremely sensitive to air and must be handled under inert atmosphere. The PBSZ was cured from 50 to 350$^\circ$C in a horizontal Schlenk furnace with a heating rate of 0.25$^\circ$C/min in flowing nitrogen. Then the PBSZ was pyrolyzed by further heat treated using a heating rate of 0.5$^\circ$C/min from 350 to 800$^\circ$C and maintained 2 h at 800$^\circ$C. Finally, further heated to 1000$^\circ$C and had a dwelling time for 2 h under nitrogen atmosphere.

2.4. Characterization
Fourier transform infrared (FT-IR) spectra were recorded in the 4000-400 cm$^{-1}$ frequency range on a Nicolet NEXUS-670, using KBr pellets. NMR experiment was performed on a a Bruker Avance 400 spectrometer. $^1$H and $^{11}$B NMR spectra were recorded in CDCl$_3$ with resonance frequencies at 400.13 and 128.37 MHz. Solid-state $^{13}$C and $^{29}$Si NMR spectra were recorded at 100.61 and 79.49 MHz, respectively, under MAS conditions. Thermo gravimetric analysis (TGA) of the as-obtained samples operating a Netzach 209 F1 Iris instrument was conducted under nitrogen atmosphere. The samples (about 10 mg) were heated from 50$^\circ$C to 900$^\circ$C with the heating rate of 10$^\circ$C/min. Gas Chromatography-Mass Spectrometer (GC-MS) of samples was analyzed by GCMS-QP-2010 instrument. The crystallization of the ceramics was characterized by X-ray diffraction (XRD) analysis (XRD Rigaku, Tokyo, Japan, Cu-K radiation) using graphite crucibles.

3. Results and discussion

3.1. Characterization of PBSZ
Structures of PBSZ were investigated via FT-IR and NMR spectroscopy. As shown in Figure 1, the signal at 3418 cm$^{-1}$ was assigned to N-H bond stretching vibration. The signals at 2959 cm$^{-1}$, 2931 cm$^{-1}$ and 2872 cm$^{-1}$ were attributed to C-H stretching. The band assigned to B-H bond was located at 1378 cm$^{-1}$ and 1338 cm$^{-1}$. Assigned to Si-C band in the Si-CH$_2$CH$_3$CH$_3$ was located at 1290 cm$^{-1}$, 1249 cm$^{-1}$ and 1194 cm$^{-1}$. A signal peak at 1460 cm$^{-1}$ was attributed to the stretching absorption of N-C and the peaks at 1168 cm$^{-1}$,1072 cm$^{-1}$ and 1023 cm$^{-1}$ were assigned to the stretching vibration band of N-C.
The characteristic peak of Si-N was observed at 892 cm\(^{-1}\) and the peak appeared at 743 cm\(^{-1}\) indicated the existence of B-N.

![FTIR Spectrum](image1.png)

**Figure 1.** FTIR spectrum of PBSZ co-polycondensed of SiCl\(_4\)/BCl\(_3\)/C\(_3\)H\(_7\)NH\(_2\).

![NMR Spectra](image2.png)

**Figure 2.** NMR spectra of PBSZ co-polycondensed of SiCl\(_4\)/BCl\(_3\)/C\(_3\)H\(_7\)NH\(_2\): (a) \(^1\)H-NMR, (b) \(^{11}\)B-NMR, (c) \(^{12}\)C-NMR, (d) \(^{29}\)Si-NMR.
Furthermore, some signals in the NMR spectra were conductive to confirming the structure of the PBSZ. Figure 2 displays the $^1$H, $^{11}$B, $^{29}$Si and $^{12}$C NMR spectra of the PBSZ. As shown in figure 2(a) of the $^1$H-NMR spectrum, the signals at 0–0.3 ppm were assigned to Si-$\text{CH}_2\text{CH}_2\text{CH}_3$; the broad peak at 0.5–1.0 ppm was assigned to N-$\text{H}$; the multiple peaks at 1.0–1.8 ppm were attributed to B-$\text{NC}_2\text{H}_4\text{Si}$ and the broad peak at 2.5–3.3 ppm was assigned to N-$\text{CH}_2\text{CH}_2\text{CH}_3$. In the $^{11}$B-NMR spectrum (figure 2(b)), only a broad peak appeared at 25–27 ppm, which due to BN structural units in six membered borazine rings [19]. In the $^{13}$C-MAS-NMR spectrum (figure 2(c)), the signals appeared at 10 ppm, 26 ppm and 44 ppm were attributed to three positional relationships of carbon in N-$\text{CH}_2\text{CH}_2\text{CH}_3$. Also comprise the structure of SiN($\text{CH}_2\text{CH}_2\text{CH}_3$)Si, BN($\text{CH}_2\text{CH}_2\text{CH}_3$)B and SiN($\text{CH}_2\text{CH}_2\text{CH}_3$)B. The difference of chemical shift of the three kinds of N-$\text{CH}_2\text{CH}_2\text{CH}_3$ was not large is due to the negative induction effect of Si, B to C was delivered by σ bond and the delivery effect of σ band was weak. Therefore, the three peaks in $^{13}$C-MAS-NMR spectrum were sharp. In the $^{29}$Si-MAS-NMR spectrum (figure 2(d)), the signal at 33 ppm was assigned to Si-N bonds and the signal at 19 ppm was assigned to Si-C bonds.

### 3.2. Ceramic conversion of PBSZ

The progress of the polymer-to-ceramic conversion of PBSZ was illustrated by TGA from room temperature to 900°C under a flowing nitrogen atmosphere. As shown in Figure 3, the mass loss of PBSZ mostly taken place in three stages. Firstly, from the room temperature to 200°C, the evaporation of low molecular weight molecules leaded to the weight loss of PBSZ. Secondly, the weight loss of PBSZ was attributed to the further cross-linking from 200°C to 500°C, accompany with the release of C$_3$H$_7$NH$_2$. At the third stage, B-N and Si-N bonds broken and released C$_3$H$_7$NH$_2$ and C$_3$H$_8$ from 500°C to 800°C. The final residual mass of PBSZ was about 64.9 wt% at 900°C.

![TGA curves of PBSZ copolycondensed of SiCl$_4$/BCl$_3$/C$_3$H$_7$NH$_2$ (N$_2$ atmosphere).](image)

To further analysis the pyrolysis process of PBSZ. The released gases at different temperature (200°C, 400°C, 550°C) during the pyrolysis were analyzed by GC-MS. As shown in figure 4, at 200°C, the released gas mainly was the release of small molecules. When the temperature enhanced to 450°C, C$_3$H$_7$NH$_2$ and little amount of oligomers released from the system. The release of C$_3$H$_7$NH$_2$ was attributed to the condensation between oligomers and the release of oligomers was resulted from the hindrance of cross-linking because of steric-inherence effect. At 550°C, besides the release of C$_3$H$_7$NH$_2$, there was C$_3$H$_8$ released from the system. This was due to the broken of B-N and Si-N.
bonds in nonreduced end of Si-NHCH$_2$CH$_2$CH$_3$ and B-NHCH$_2$CH$_2$CH$_3$. As we can see, the GC-MS results agreed with the TGA analysis.

Figure 5 shown the SEM microstructure of the SiBNC ceramics pyrolyzed at 800°C. It could be seen that the SiBNC granulation was nearly global and on the surface formed a dense layer.

**Figure 4.** GC-MS spectra of PBSZ pyrolyzed at different time (N$_2$ atmosphere): (a) 200°C; (b) 450°C; (a) 650°C.

**Figure 5.** SEM of the SiBNC ceramics pyrolyzed at 800°C.
To investigate crystallization behavior, PBSZ pyrolyzed at different temperatures for 6 h were analyzed by XRD. As shown in figure 6, the pyrolyzed samples from 1000 to 1600°C were all exhibited only an broad peak at $\theta=22.5^\circ$, assigned to amorphous silicide, which indicated the high temperature stability and crystallization resistance of SiBNC ceramics.

![XRD spectra](image)

**Figure 6.** XRD spectra of polymer-derived ceramics pyrolyzed at different temperatures for 6 h: (a) 1000°C; (b) 1400°C; (a) 1600°C.

### 4. Conclusion

This study demonstrates the possibility of producing high performance SiBNC ceramic derived from a novel polymeric precursor. This polymeric precursor was synthesized in one-step by co-condensation of $\text{BCl}_3$, $\text{SiCl}_4$ and $\text{C}_3\text{H}_7\text{NH}_2$. FT-IR and NMR analysis indicated that it contains B-N, Si-N, N-H and N-CH$_2$CH$_2$CH$_3$ bonds. The ceramic yield of this polymeric precursor is about 64.9 wt% after annealed at 900°C in nitrogen atmosphere. XRD spectra illustrate that the obtained SiBNC ceramic exhibit high temperature stability and keep amorphous after annealed at 1600°C in nitrogen atmosphere.

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