



Cite this: *RSC Adv.*, 2022, 12, 8154

# High temperature structure evolution of SiBZrOC quinary polymer derived ceramics

Chen Liu, <sup>\*ab</sup> Changqing Hong,<sup>b</sup> Xinwei Wang<sup>\*a</sup> and Jiecai Han<sup>b</sup>

SiBZrOC quinary ceramics were obtained through the modification of a SiOC precursor with B(OH)<sub>3</sub> and Zr(OnPr)<sub>4</sub>. The results showed that both B and Zr atoms were involved in the SiOC network through Si–O–B and Si–O–Zr bonds, respectively. The combined effects of B and Zr on the chemical structure and the thermal stability of the SiBZrOC system were investigated in detail. The sp<sup>3</sup>–C/Si ratio of SiBZrOC ceramics was between the values for SiZrOC and SiBOC. The presence of B promotes the crystallization of t-ZrO<sub>2</sub>, which precipitated at 1000 °C and transformed to m-ZrO<sub>2</sub> at 1400 °C. At 1600 °C, ZrO<sub>2</sub> reacted with the matrix and formed ZrSiO<sub>4</sub>, which consumed SiO<sub>2</sub> and thus inhibited the carbothermal reaction. The very small I(D)/I(G) ratio of 0.13 in the Raman spectra indicated the high graphitization of free carbon in SiBZrOC ceramics, which was observed by TEM with 10–20 graphene layers. The SiBZrOC ceramics showed excellent thermal stability in argon at 1600 °C for 5 h with a mass loss of 6%. Both the formation of ZrSiO<sub>4</sub> and the highly graphitized free carbon play important roles in inhibiting the carbothermal reaction and thus improving the thermal stability of SiBZrOC ceramics.

Received 12th November 2021

Accepted 31st January 2022

DOI: 10.1039/d1ra08208f

rsc.li/rsc-advances

## Introduction

Polymer-derived ceramics (PDCs) are attractive candidates for use under extreme conditions owing to their high strength, creep and thermal shock resistance, as well as stability in oxidative and corrosive environments. They are X-ray amorphous and comprised of nanodomains of different structures and compositions, obtained by the thermal decomposition of organic polymers. The most well-known classes of PDCs are the ternary systems SiCN and SiCO as well as the quaternary systems SiCNO, SiBCN, SiBCO, SiAlCN, and SiAlCO.<sup>1–4</sup> Usually, quaternary ceramics exhibit improved mechanical and thermal properties as compared to those of the ternary materials. Recent investigations have shown that the high temperature stability in terms of decomposition for the SiBCN ceramics can reach 2200 °C.<sup>5</sup>

The fabrication processes of these materials involve the preparation of precursors, pyrolysis and sintering. The modification of the precursor with B<sup>6–8</sup> and metallic elements such as Al,<sup>9–11</sup> Ti,<sup>12,13</sup> or Zr<sup>14–16</sup> Hf,<sup>17–20</sup> allows the design and controlled synthesis of multifunctional PDC materials with tailored properties. They are typically prepared by modifying precursors with metal alkoxides and subsequent ceramization, leading to SiOC/SiCN nanocomposites containing a finely dispersed metal oxide nanodomains. The nanodomains may significantly influence

the microstructure and physical properties of these ceramics on a large scale, especially when the domains differ in their chemistry, electrical conductivity, and mechanical properties.<sup>21–25</sup>

Though early work already strongly suggested the nanoscale heterogeneity both in SiCO- and SiCN-based materials, the detailed chemical and structural nature of the quinary PDCs remained elusive. In previous work,<sup>26,27</sup> we prepared the B-modified and Zr-modified SiOC precursor through the chemical reactions of hybrid alkoxysilanes with boric acid and Zr(OnPr)<sub>4</sub>, respectively. The results showed that the effects of B and Zr are contrary on some cases, such as the precipitation of SiC and the graphitization of free carbon. In this work, we synthesized a SiBZrOC quinary precursor by using the same raw materials and compared with previous work, to study the combined effects of B and Zr on the polymer-to-ceramic transformation processes and the microstructure evolution of SiBZrOC materials. Various characterization techniques such as NMR and Raman spectroscopy, X-ray diffraction, as well as TEM were used to study the structure of the metallo-organic precursor and the nanocomposites.<sup>28–33</sup>

## Experimental

Methyltriethoxysilane (MTES), methyldiethoxysilane (MDES), boric acid (B(OH)<sub>3</sub>) and Zr(OnPr)<sub>4</sub> (Alfa Aesar, 70 wt% in propanol) were used as the starting raw materials. MTES, MDES and B(OH)<sub>3</sub> was mixed with the molar ratio of MTES/MDES = 3 and B : Si = 0.4. The mixture was stirred until complete dissolution. The appropriate amount of Zr(OnPr)<sub>4</sub> was then added to the

<sup>a</sup>Laboratory for Space Environment and Physical Science, Harbin Institute of Technology, Harbin, 150001, PR China. E-mail: liuchen2016@hit.edu.cn; xinweiwang@hit.edu.cn

<sup>b</sup>National Key Laboratory of Science and Technology on Advanced Composites in Special Environments, Harbin Institute of Technology, Harbin 150001, PR China



prehydrolyzed solution under fast stirring with the molar ratio of Zr : Si = 0.2. The mixture was obtained and heated at 80 °C for 1 day for gelation. The SiBzrOC gel were dried at 80 °C for 2 days, grounded and finally sieved to <75 μm. The SiBzrOC precursor was finally obtained and pyrolyzed in a tube furnace with a heating rate of 5 °C min<sup>-1</sup> in flowing argon gas, at 1000 °C, 1200 °C, 1400 °C, and 1600 °C for 1 h, followed by furnace cooling to ambient temperature.

TG were performed on the xerogels using a PerkinElmer differential scanning calorimeter from room temperature to 1400 °C at a heating rate of 10 °C min<sup>-1</sup> under argon atmosphere. FTIR spectra of the precursor were recorded between 4000 and 400 cm<sup>-1</sup> on a PerkinElmer Spectrum One FTIR spectrometer. NMR spectrum of precursor and ceramics was collected using a 4 mm Bruker CP MAS probe and a Bruker Ultrashield 300 MHz solid-state spectrometer. <sup>29</sup>Si CP MAS Powder samples were taken in ZrO<sub>2</sub> rotors and were spun at a rate of 5 kHz. The spectrum was collected using 30° pulses length of 4 μs and 2 s recycle delay. For each <sup>29</sup>Si NMR spectrum, 4000–90 000 transients were accumulated with a spectral width of 59 kHz. XRD patterns of ceramics were collected using a Philips X'Pert diffractometer with Cu Kα radiation. A 2θ range of 10–90° was scanned with a step size of 0.05°. Raman spectra were collected on a Raman Station (B&WTEK, BWS435-532SY) with a near infrared laser operating at 532 nm. The microstructure of the ceramics was observed using scanning electron microscopy (Helios Nanolab600i). A Philips-FEI Tecnai G2 F30 instrument was used to perform TEM investigations on the ceramic powders dispersed on copper grid.

## Results and discussion

The TG/DTG curves of SiBzrOC precursor was shown in Fig. 1. The weight loss occurred mainly in three stages in the temperature intervals 50–200 °C, 200–500 °C, and 500–800 °C, respectively. The DTG curve shows an intense peak at 100 °C corresponding to a weight loss of 6 wt%, which is attributed to the loss of water and ethanol. The second weight loss of 7 wt% in the range of 200–500 °C, is probably related to the release of boric acid, H<sub>2</sub>, and CH<sub>4</sub> as the predominant volatiles. In the third step, the weight loss of 4% is mainly due to the evolution of methane Si-CH<sub>3</sub>. At above 800 °C, the weight remains unchanged and the ceramic yield was found to be 83%.

Fig. 2 shows the infrared spectra of SiBzrOC precursor and ceramics pyrolyzed at 1000 to 1600 °C. All the spectra show the characteristic peak of Si-O-Si bond between 1000 and 1130 cm<sup>-1</sup>, which is split into two bands at 1035 and 1125 cm<sup>-1</sup>, indicating the high degree of polymerization of the precursors. Si-O-Zr bond at 905 cm<sup>-1</sup> was detected in the precursor formed through reactions (1) and (2), whilst disappeared in the ceramics owing to the redistribution reaction between Si-O and Zr-O bonds and thus formed Zr-O-Zr bonds. Si-O-B bond at 875 cm<sup>-1</sup> was found in the ceramics, whilst absent in the precursor. This is probably because the Si-O-B bond has been formed through reaction (3) in the precursor, but covered up by the Si-O-Zr bond in the ceramics. The FTIR results confirmed

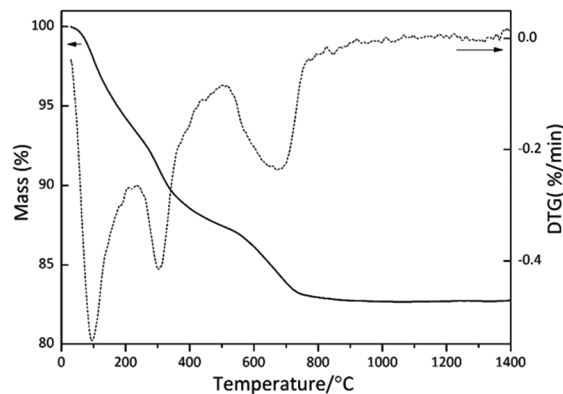


Fig. 1 TG curves of SiBzrOC precursor.

that both B and Zr were involved in the siloxane network in the SiOC network in the ceramics.

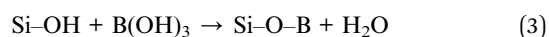
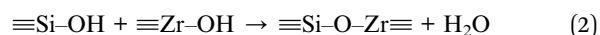
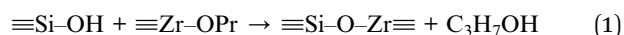


Fig. 3 shows the <sup>29</sup>Si NMR spectra of SiOC, SiBOC, SiZrOC and SiBzrOC precursor. The spectra of SiOC and SiBOC precursor present a sharp signal at -69 ppm assigned to SiCO<sub>3</sub> units and another peak at -39 ppm due to HSiCO<sub>2</sub> units, whilst the latter was absent in SiZrOC and SiBzrOC precursor, revealing that the Si-H bonds has been transformed into Si-O bonds through reactions (4) and (5) in Zr-containing precursor.<sup>26</sup> Moreover, the SiCO<sub>3</sub> peaks in SiZrOC and SiBzrOC precursor were simulated with two Gaussian peaks at -62.7 and -69 ppm, which were assigned to the SiCO<sub>3</sub> units with and without Si-O-Zr bonds, respectively. The former unit accounts for 50% in SiBzrOC, which is obviously lower than the 74% in SiZrOC ceramics,<sup>26</sup> suggesting that the SiCO<sub>3</sub> units with Si-O-B bond in SiBzrOC accounts for 24% at most. The formation of

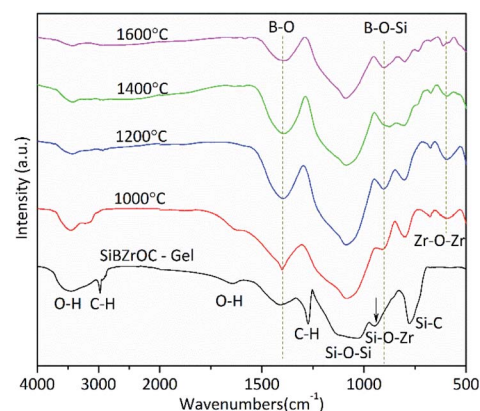


Fig. 2 Infrared spectra of SiBzrOC xerogel and ceramics pyrolyzed at various temperatures.



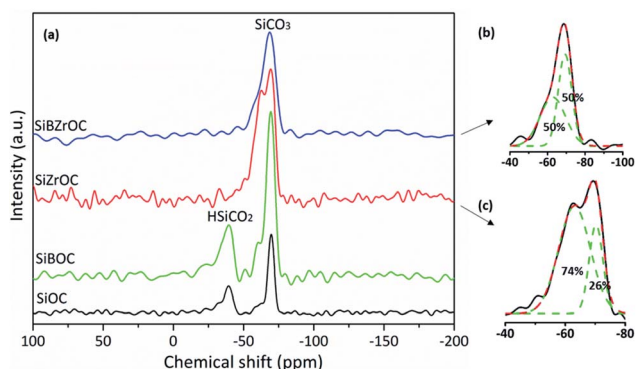
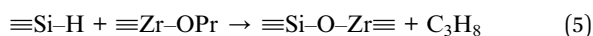


Fig. 3  $^{29}\text{Si}$  MAS NMR spectra of SiOC, SiBOC, SiZrOC and SiBZrOC precursor.<sup>26,27</sup>

Si–O–B bonds consumed a part of Si–O bonds and thus decreased the content of Si–O–Zr bonds. Combined with the FTIR results, it is confirmed that Zr and B was distributed uniformly in the SiOC network at atomic scale.



As comparison, TG curves of SiOC, SiBOC and SiZrOC<sup>26,27</sup> precursor were shown in Fig. 4. The ceramic yield of SiBZrOC is 83%, much lower than the 93% of SiBOC, and slightly higher than the 81% of SiZrOC. This is probably because the formation of Si–O–B bond lead to a more interconnected gel network,<sup>34</sup> and thus higher ceramic yield in B-containing precursors. Compared with SiZrOC, the ceramic yield of SiBZrOC was slightly improved owing to the Si–O–B bonds formed through the 24% Si–O bonds.

The  $^{29}\text{Si}$  MAS NMR spectra of SiBZrOC ceramics pyrolyzed at various temperature are presented in Fig. 5. All the spectra show the resonance peaks of  $\text{SiO}_4$  ( $\delta = -110$  ppm) and  $\text{SiC}_4$  ( $\delta = -15$  ppm) units, resulting from the redistribution reaction between

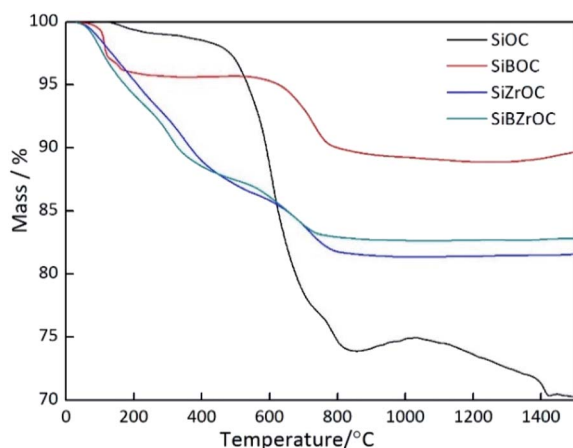


Fig. 4 TG curves of SiOC, SiBOC, SiZrOC and SiBZrOC ceramics.<sup>26,27</sup>

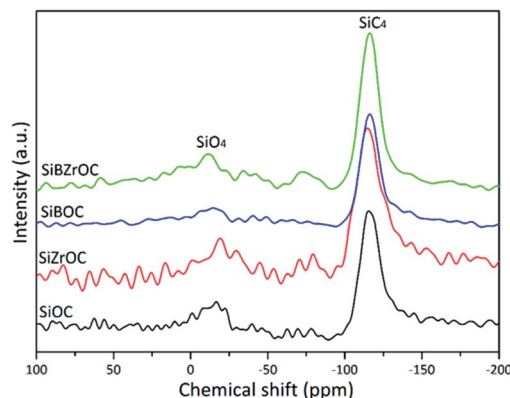


Fig. 5  $^{29}\text{Si}$  MAS NMR spectra of SiOC, SiZrOC, SiBOC and SiBZrOC ceramics pyrolyzed at 1200 °C.<sup>26,27</sup>

Si–O and Si–C bond. The  $\text{sp}^3\text{-C/Si}$  ratio of the four ceramics were calculated according to the peak area of  $\text{SiO}_4$  and  $\text{SiC}_4$ , listed in Table 1. It can be seen that the  $\text{sp}^3\text{-C/Si}$  ratio of SiZrOC ceramics is 0.12, lower than the 0.16 of SiOC ceramics, which is attributed to the addition of Zr atom, leading to a decrease in the thermal stability of Si–C bond.<sup>15</sup> The SiBOC ceramics is 0.27, much higher than that of SiOC ceramics.<sup>26</sup> This is because the presence of Si–H groups in the precursor promotes the insertion of C into SiCO network<sup>26</sup> and the redistribution reaction between B–C and Si–O bond could also lead to the increase of  $\text{sp}^3\text{-C}$ .<sup>35</sup> The  $\text{sp}^3\text{-C/Si}$  ratio in SiBZrOC ceramics is 0.22, between the value of SiBOC and SiZrOC, resulting from the combined effects of B and Zr.

XRD patterns of SiBZrOC ceramics pyrolyzed at various temperatures are presented in Fig. 6. At 1000 and 1200 °C,  $t\text{-ZrO}_2$  phase is found as the only crystalline phase in SiBZrOC ceramics. Small amounts of  $m\text{-ZrO}_2$  were detected at 1400 °C, which was formed through the phase transformation from  $t\text{-ZrO}_2$  during cooling down when the  $t\text{-ZrO}_2$  grew up to the critical size.<sup>26</sup> It can be seen that the phase transformation temperature for SiBZrOC is 1400 °C, much lower than the 1600 °C for SiZrOC,<sup>26</sup> revealing the growth of  $t\text{-ZrO}_2$  in SiBZrOC are faster than SiZrOC. Therefore, it can be concluded that the addition of B facilitates the growth of  $t\text{-ZrO}_2$  crystallites. Moreover,  $\text{ZrSiO}_4$  was found at 1600 °C, formed by the reaction of zirconia with amorphous silica in the matrix.

Fig. 7 shows the Raman spectra of SiBZrOC ceramics pyrolyzed at various temperatures. All the Raman spectra show two characteristic features of disordered graphitic forms of carbon: the D band at about  $1350\text{ cm}^{-1}$  due to the defects and the G

Table 1 Calculated  $\text{sp}^3\text{-C/Si}$  ratio of SiOC SiZrOC<sup>26</sup> SiBOC and SiBZrOC ceramics pyrolyzed at 1200 °C

Ceramics	$\text{sp}^3\text{-C/Si}$
SiOC	0.16
SiZrOC	0.12
SiBOC	0.27
SiBZrOC	0.22

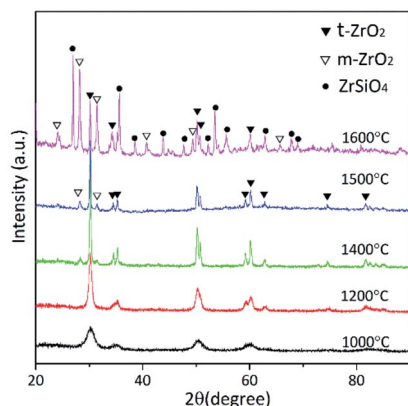


Fig. 6 XRD patterns of SiBZrOC ceramics pyrolyzed at various temperatures.

band at  $1590\text{ cm}^{-1}$  related to in-plane bond stretching of  $\text{sp}^2$  carbon. The G band narrows from  $47\text{ cm}^{-1}$  to  $21\text{ cm}^{-1}$  and shifts to the lower frequencies, suggesting the increasing graphitization of free carbon with temperature.

The D band appears due to the  $\text{A}_{1g}$  breathing mode and requires a defect for its activation. In our case, the D band is possibly related to carbon dangling bonds or  $\text{sp}^3$  carbon atoms. The intensity ratio of D and G bands,  $I(\text{D})/I(\text{G})$ , reflects the graphitization of carbon materials, and it decreased with increasing graphitization. The diameter of free carbon cluster can be calculated using eqn (6),<sup>36,37</sup> shown in Table 2. The intensity of G band increases dramatically at above  $1600^\circ\text{C}$ , and accordingly the  $I(\text{D})/I(\text{G})$  rapidly decreases to 0.13 at  $1600^\circ\text{C}$ , which leads to a large  $L_a$  of 38.1 nm.

$$\frac{I_D}{I_G} = \frac{C(\lambda)}{L_a} \quad (6)$$

Usually, the value of  $I(\text{D})/I(\text{G})$  for SiBOC ceramics is more than 1 at below  $1600^\circ\text{C}$ . In our case, the intensity of G band increases dramatically at above  $1400^\circ\text{C}$ , and accordingly the

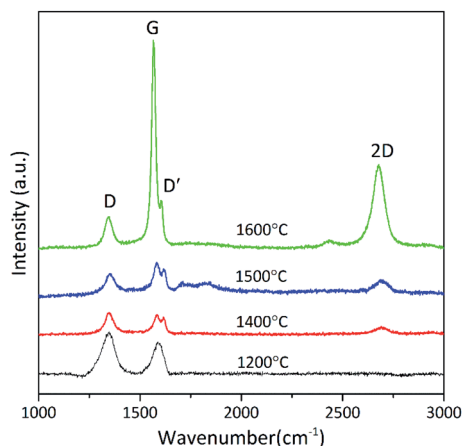


Fig. 7 Raman spectra of SiBZrOC ceramics pyrolyzed at various temperatures.

Table 2 Raman spectra parameters for SiBZrOC ceramics pyrolyzed at various temperatures

Temperature ( $^\circ\text{C}$ )	$I(\text{D})/I(\text{G})$	$\omega_G$ ( $\text{cm}^{-1}$ )	FWHM ( $\text{cm}^{-1}$ )	$L_a$ (nm)
1200	1.3	1598	47	3.8
1400	1.2	1583	39	4.1
1500	0.69	1583	31	7.2
1600	0.13	1576	21	38.1

$I(\text{D})/I(\text{G})$  decreases to 0.13 at  $1600^\circ\text{C}$ , which is far smaller than that in SiZrOC ceramics ( $I(\text{D})/I(\text{G}) = 1.4$ ). The results indicate that the addition of B significantly promotes the graphitization and the growth of free carbon cluster. This is probably owing to the partial substitution of C with B atoms, which could increase the crystallinity of carbon.<sup>37,38</sup> The D' bands at  $1608\text{ cm}^{-1}$  is considered to be the fingerprint of  $\text{BC}_3$  site formed by the substitution of B for C atom.<sup>9</sup> This substitution of C by B atom introduces a local distortion within the graphite layer planes, and thus formed crystalline defects. The electron deficiency of boron with respect to carbon causes a decrease in the repulsive interaction between the  $\pi$ -electron clouds of adjacent graphene layers, allowing these layers to come closer together, and thus lead to the increased graphitization degree of free carbon.<sup>37,38</sup>

Backscattered electron images of the fracture of SiBZrOC ceramics pyrolyzed at  $1000^\circ\text{C}$ ,  $1200^\circ\text{C}$ ,  $1400^\circ\text{C}$  and  $1600^\circ\text{C}$  are shown in Fig. 8. Combined with XRD results, the white grains precipitated at  $1200^\circ\text{C}$  with a size of 30–80 nm were t-ZrO<sub>2</sub>. The spherical grains uniformly dispersed in the matrix and grew up to 200–350 nm at  $1600^\circ\text{C}$ , which were supposed to be t-ZrO<sub>2</sub>, m-ZrO<sub>2</sub> and ZrSiO<sub>4</sub> crystallites, according to XRD results.

Fig. 9 shows the TEM images and the corresponding diffraction patterns of SiBZrOC ceramics. The oval particle in the middle and the irregular particles in the upper are

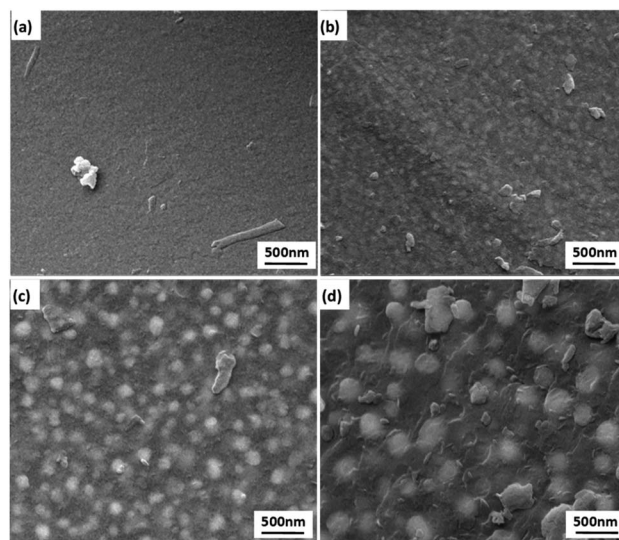


Fig. 8 SEM images of SiBZrOC ceramics pyrolyzed at (a)  $1000^\circ\text{C}$ , (b)  $1200^\circ\text{C}$ , (c)  $1400^\circ\text{C}$  and (d)  $1600^\circ\text{C}$ .





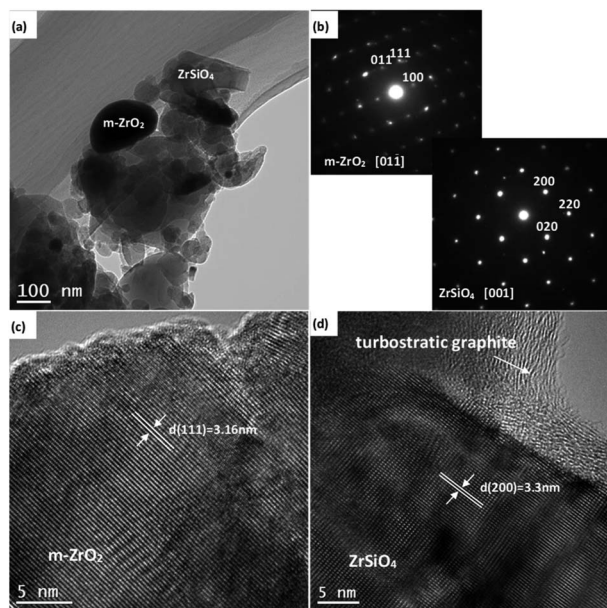


Fig. 9 TEM images of SiBzrOC ceramics pyrolyzed at 1600 °C. (a) Bright field image, (b) diffraction patterns, (c) and (d) high-resolution micrographs.

Table 3 Mass loss of SiZrOC and SiBzrOC ceramics pyrolyzed at 1200 °C after annealing in argon at 1400 °C, 1500 °C and 1600 °C for 5 h

Temperature (°C)	Mass loss	
	SiZrOC	SiBzrOC
1400	1%	1%
1500	4%	3%
1600	10%	6%

determined to be m-ZrO<sub>2</sub> and the ZrSiO<sub>4</sub>, respectively, through the diffraction patterns in Fig. 9(b). They are well-crystallized as shown in the HRTEM images Fig. 8(c) and (d). Fig. 8(d) shows the typical turbostratic structure of free carbon with 10–20 graphene layers, which is rarely found in the SiZrOC ceramics.<sup>26</sup> It is confirmed that the addition of B significantly promotes the graphitization of free carbon.

Table 3 shows the mass loss of SiZrOC and SiBzrOC ceramics pyrolyzed at 1200 °C after annealing in argon at 1400 °C, 1500 °C and 1600 °C for 5 h. The SiBzrOC sample shows a mass loss of 6% compared with the SiZrOC sample of 10%, indicating the enhanced thermal stability in SiBzrOC. This can be attributed to the highly graphitized free carbon and the reaction of SiO<sub>2</sub> and ZrO<sub>2</sub>, which both inhibit the carbothermal reaction between SiO<sub>2</sub> and free carbon.

## Conclusions

SiBzrOC quinary ceramics was prepared through the chemical reactions of hybrid alkoxysilanes with boric acid and Zr(OnPr)<sub>4</sub>. Si–O–Zr and Si–O–B bonds were formed in the precursor and

a high ceramic yield of 83% was achieved. The addition of B promoted the crystallization of ZrO<sub>2</sub> and the graphitization of free carbon, as well as increased the sp<sup>3</sup>–C/Si ratio. t-ZrO<sub>2</sub> precipitated at 1200 °C with a size of 30–80 nm, reacted with the matrix and thus formed ZrSiO<sub>4</sub> at 1600 °C. Turbostratic graphite with 10–20 graphene layers was clearly observed in TEM. The SiBzrOC sample showed excellent thermal stability in argon at 1600 °C for 5 h with a mass loss of 6%. Both the formation of ZrSiO<sub>4</sub> and the highly graphitized free carbon inhibited the carbothermal reaction and thus improved the thermal stability of SiBzrOC ceramics.

## Conflicts of interest

The authors confirm that the content of this article has no conflicts of interest.

## Acknowledgements

This research is supported by the Science Foundation of National Key Laboratory of Science and Technology on Advanced Composites in Special Environments, the National Natural Science Foundation of China (51602076) and China Postdoctoral Science Foundation Grant (2016M601426).

## Notes and references

- 1 S. Fu, M. Zhu and Y. Zhu, *J. Adv. Ceram.*, 2019, **8**, 457–478.
- 2 G. Mera, A. Navrotsky and S. Sen, *J. Mater. Chem. A*, 2013, **1**, 3826–3836.
- 3 E. Erdem, V. Mass, A. Gembus, A. Schulz, V. Liebau-Kunzmann, C. Fasel, R. Riedelf and R. Eichel, *Phys. Chem. Chem. Phys.*, 2009, **11**, 5628–5633.
- 4 I. Menapace, G. Mera, R. Riedel, E. Erdem, R. Eichel, A. Pauletti and G. A. Appleby, *J. Mater. Sci.*, 2008, **43**, 5790–5796.
- 5 P. Zhang, D. Jia, Z. Yang, X. Duan and Y. Zhou, *J. Adv. Ceram.*, 2012, **1**, 157–178.
- 6 G. D. Soraru, N. Dallabona, C. Gervais and F. Babonneau, *Chem. Mater.*, 1999, **11**, 910–919.
- 7 R. Pena-Alonso, G. Mariotto, C. Gervais, F. Babonneau and G. D. Soraru, *Chem. Mater.*, 2007, **19**, 5694–5702.
- 8 A. Schiavon, C. Gervais, F. Babonneau and G. D. Soraru, *J. Am. Ceram. Soc.*, 2004, **87**, 203–208.
- 9 B. Julian, C. Gervais, E. Cordoncillo, P. Escribano, F. Babonneau and C. Sanchez, *Chem. Mater.*, 2003, **15**, 3026–3034.
- 10 X. Li and M. J. Edirisinghe, *Chem. Mater.*, 2004, **16**, 1111–1119.
- 11 T. Xu, Q. Ma and Z. Chen, *Mater. Lett.*, 2012, **66**, 364–366.
- 12 L. Crouzet, D. Leclercq, P. H. Mutin and A. Vioux, *Chem. Mater.*, 2003, **15**, 1530–1534.
- 13 S. Dire, R. Ceccato and F. Babonneau, *J. Sol-Gel Sci. Technol.*, 2005, **34**, 53–62.
- 14 E. Ionescu, C. Linck, C. Fasel, M. Müller, H. J. Kleebe and R. Riedel, *J. Am. Ceram. Soc.*, 2010, **93**, 241–250.



- 15 S. Dire, R. Camprostrini and R. Ceccato, *Chem. Mater.*, 1998, **10**, 268–278.
- 16 S. Dire, R. Ceccato, S. Gialanella and F. Babonneau, *J. Eur. Ceram. Soc.*, 1999, **19**, 2849–2858.
- 17 E. Ionescu, B. Papendorf, H. Kleebe, F. Poli, K. Müller and R. Riedel, *J. Am. Ceram. Soc.*, 2010, **93**, 1774–1782.
- 18 E. Ionescu, B. Papendorf, H. Kleebe, F. Poli, K. Müller and R. Riedel, *J. Am. Ceram. Soc.*, 2010, **9**, 1783–1789.
- 19 H. Kleebe, K. Nonnenmacher, E. Ionescu and R. Riedel, *J. Am. Ceram. Soc.*, 2012, **95**, 2290–2297.
- 20 K. Nonnenmacher, H. Kleebe, J. Rohrer, E. Ionescu and R. Riedel, *J. Am. Ceram. Soc.*, 2013, **96**, 2058–2060.
- 21 B. Papendorf, K. Nonnenmacher, E. Ionescu, H. Kleebe and R. Riedel, *Small*, 2011, **7**, 970–978.
- 22 E. Ionescu, H. Kleebe and R. Riedel, *Chem. Soc. Rev.*, 2012, **41**, 5032–5052.
- 23 F. Li, X. Huang, J. X. Liu and G. J. Zhang, *J. Adv. Ceram.*, 2020, **9**, 1–16.
- 24 P. Colombo, G. Mera, R. Riedel and G. D. Soraru, *J. Am. Ceram. Soc.*, 2010, **93**, 1805–1837.
- 25 N. Srinivasan, S. Ravindran and K. Ravi, *J. Am. Ceram. Soc.*, 2013, **2**, 318–324.
- 26 C. Liu, R. Pan, C. Hong, X. H. Zhang, W. Han, J. Han and S. Du, *J. Eur. Ceram. Soc.*, 2016, **36**, 395–402.
- 27 X. Zhang, C. Liu, C. Hong, J. Han, W. Han and S. Du, *Ceram. Int.*, 2015, **41**, 15292–15296.
- 28 S. J. Widgeon, S. Sen, G. Mera, E. Ionescu, R. Riedel and A. Navrotsky, *Chem. Mater.*, 2010, **22**, 6221–6228.
- 29 S. J. Widgeon, G. Mera, Y. Gao, E. Stoyanov, S. Sen, A. Navrotsky and R. Riedel, *Chem. Mater.*, 2012, **24**, 1181–1191.
- 30 G. Mera, A. Navrotsky, S. Sen, H. Kleebe and R. Riedel, *J. Mater. Chem. A*, 2013, **1**, 3826–3836.
- 31 G. Hasegawa, K. Kanamori, K. Nakanishi and T. Hanada, *J. Mater. Chem.*, 2009, **19**, 7716–7720.
- 32 G. Hasegawa, K. Kanamori, K. Nakanishi and T. Hanada, *Chem. Mater.*, 2010, **22**, 2541–2547.
- 33 Y. Shi, Y. Wan, Y. Zhai, R. Liu, Y. Meng, B. Tu and D. Zhao, *Chem. Mater.*, 2007, **19**, 1761–1771.
- 34 G. D. Soraru, R. Camprostrini and S. Maurina, *J. Am. Ceram. Soc.*, 1997, **80**, 999–1004.
- 35 C. Gervais, F. Babonneau, N. Dallabonna and G. D. Soraru, *J. Am. Ceram. Soc.*, 2001, **84**, 2160–2164.
- 36 T. Jiang, Y. Wang, Y. Wang and N. Orlovskaya, *J. Am. Ceram. Soc.*, 2009, **92**, 2455–2458.
- 37 M. Li, L. Cheng, F. Ye, C. Zhang and J. Zhou, *J. Adv. Ceram.*, 2021, **10**, 1256–1272.
- 38 Y. J. Lee, *J. Nucl. Mater.*, 2004, **325**, 174–179.

