

Polymer-derived SiBCN ceramic pressure sensor with excellent sensing performance

Gang SHAO^{a,*}, Junpeng JIANG^a, Mingjie JIANG^a, Jie SU^a, Wen LIU^{a,*},
Hailong WANG^a, Hongliang XU^a, Hongxia LU^a, Rui ZHANG^{a,b}

^aSchool of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

^bProvincial Key Laboratory of Aviation Materials and Application Technology, Zhengzhou University of Aeronautics, Zhengzhou 450046, China

Received: January 27, 2020; Revised: March 4, 2020; Accepted: March 21, 2020

© The Author(s) 2020.

Abstract: Pressure measurement with excellent stability and long time durability is highly desired, especially at high temperature and harsh environments. A polymer-derived silicoboron carbonitride (SiBCN) ceramic pressure sensor with excellent stability, accuracy, and repeatability is designed based on the giant piezoresistivity of SiBCN ceramics. The SiBCN ceramic sensor was packaged in a stainless steel case and tested using half Wheatstone bridge with the uniaxial pressure up to 10 MPa. The SiBCN ceramic showed a remarkable piezoresistive effect with the gauge factor (K) as high as 5500. The output voltage of packed SiBCN ceramic sensor changes monotonically and smoothly versus external pressure. The as received SiBCN pressure sensor possesses features of short response time, excellent repeatability, stability, sensitivity, and accuracy. Taking the excellent high temperature thermo-mechanical properties of polymer-derived SiBCN ceramics (e.g., high temperature stability, oxidation/corrosion resistance) into account, SiBCN ceramic sensor has significant potential for pressure measurement at high temperature and harsh environments.

Keywords: polymer-derived ceramics (PDCs); silicoboron carbonitride (SiBCN) ceramic pressure sensor; piezoresistivity; high temperature and harsh environment sensor

1 Introduction

Pressure sensor is highly desired to provide online health monitoring and improve the safety of modern industry, especially for those of high temperature and harsh environments such as turbine engines and coal gasification [1,2]. Sensors based on piezoresistive behavior of materials are one of the most adopted ones

for pressure sensing due to its facile sensor design and easy fabrication. However, due to the serious drift effect and degradation at high temperature, the polymer based piezoresistive pressure sensors are not suitable for pressure measurement at the circumstance of high temperature and/or room temperature for long time [3–5]. On the contrary, ceramic based piezoresistive pressure sensors possess excellent stability and long time durability [6,7], even at high temperatures [8–10]. Nevertheless, poor sensitivity is the obvious drawback of these ceramic based pressure sensors due to their limited piezoresistive coefficient (gauge factor, K) [11,12].

* Corresponding authors.

E-mail: G. Shao, gang_shao@zzu.edu.cn;

W. Liu, liuwen@zzu.edu.cn

Polymer-derived ceramics (PDCs) obtained by thermal decomposition of polymeric precursor own excellent thermal stability up to 2000 °C [13], and oxidation resistance/corrosion resistance (better than that of SiC and Si₃N₄) [14–16]. Meanwhile, PDCs exhibit extreme high piezoresistivity with *K* up to 4000–7000 [17–19], which is much higher than that of the commonly used ceramics of Si (*K* = 37.5) [11] and SiC (*K* = 30) [12]. Therefore, PDCs are a promising candidate for pressure sensing with remarkable sensitivity and stability, especially at high temperature and harsh environments. These unique properties are ascribed to their unique microstructures with a nanodomain structure consisting of Si-based amorphous matrix and highly disordered carbon clusters, named free-carbon phase [20,21]. Specially, silicoboron carbonitride (SiBCN) is one of the most promising PDCs for ultra-high-temperature applications, due to its excellent stability up to 2000 °C and prominent creep resistance [13]. For its superior properties, SiBCN ceramics have been extensively investigated including synthesis [22–24], structural evolution [25–28], high temperature stability [13,29,30], etc. However, the piezoresistivity and pressure sensing ability of SiBCN ceramic have not been reported yet.

In this study, a piezoresistive pressure sensor made of polymer-derived SiBCN ceramic is reported for the first time. The piezoresistivity of SiBCN ceramic sensor and relative sensing performance of stability, repeatability, and response time were discussed, indicating the promising potential application at high temperature and harsh environments of SiBCN ceramic pressure sensor.

2 Experimental

2.1 Fabrication of SiBCN ceramic sensor head

The SiBCN ceramic sensor head was synthesized by using a commercially available liquid precursor, polyborosilazane (PSNB, Institute of Chemistry, Chinese Academy of Sciences, Beijing, China). Briefly, the obtained PSNB precursor was cross-linked by heat-treatment at 200 °C for 4 h in vacuum oven without any other curing agents to acquire infusible solid, which was subsequently ground to fine powder of ~1 μm by high energy ball milling (8000M, SPEX SamplePrep, United States). Then the powder was pressed into disks with the size of φ12 mm × 3 mm using uniaxial

pressing at 20 MPa for 2 min. The disc like green bodies were pyrolyzed at 1000 °C for 4 h in a tube furnace with the heating and cooling rate of 5 °C/min to yield amorphous SiBCN ceramics. Finally, these ceramic samples were post-treated at temperature of 1300 °C for 4 h to tune the piezoresistivity of SiBCN ceramics. The entire pyrolysis and post-treatment process were performed in the flowing of ultra-high purity N₂ to minimize possible oxygen contamination.

The SiBCN ceramic pressure sensor head was cut from the above mentioned sample with dimension of ~6 mm × 6 mm × 1.7 mm. For piezoresistivity characterization and sensor test purpose, both square surfaces (6 mm × 6 mm) of SiBCN ceramic sensor head were polished to 1 μm finish and coated with silver paste (5002-AB, SPI, Pennsylvania, USA) as electrodes. Then a universal testing system (ZQ-990B, Zhiqu, Dongguan, Guangdong, China) was used to apply compressive stress. The resistance was measured by a high temperature insulation resistance testing system (HRMS-900, Partulab, Wuhan, Hubei, China).

2.2 Sensor design, assembling, and test setup

In order to convert the output resistance change into voltage signal, a half Wheatstone bridge circuit is designed, as shown in Fig. 1, which composed of the SiBCN ceramic sensor head (*R*) and standard resistance (*R*₀) for matching purpose.

A constant voltage of *V*₀ = 9 V was supplied by the laboratory dedicated electronic regulated power source, and the relative output voltage (*V*_{out}) was recorded by digital multimeter, as described by

$$V_{out} = V_0 R_0 / (R_0 + R) \tag{1}$$

The range of output voltage (*V*_r) can be expressed as

$$V_r = V_{max} - V_{min} \\ = V_0 R_0 / (R_0 + R_{min}) - V_0 R_0 / (R_0 + R_{max}) \tag{2}$$

where *V*_{max} and *V*_{min} are the voltages of the matched resistor when the sensor head with the minimum and

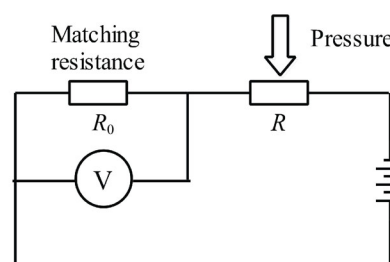


Fig. 1 Circuit of the designed pressure sensor.

maximum resistance, R_{\min} and R_{\max} , respectively (corresponding to the maximum and minimum pressure applied on the sensor head).

Then the resistance of matching resistor can be selected by optimizing the sensitivity of the sensor by Eq. (3):

$$\partial V_r / \partial R_0 = 0 \tag{3}$$

Solving Eq. (3), the optimal resistance of the matching resistor R_0 can be calculated by Eq. (4) to be 1 MΩ, with the resistance of R_{\max} and R_{\min} to be 2.92 and 2.76 MΩ, corresponding to the maximum (7 MPa) and the minimum (0 MPa) pressure applied on the sensor (size of the sensor head: ~6 mm × 6 mm × 1.7 mm).

$$R_0 = \frac{R_{\min} \sqrt{R_{\max}} - R_{\max} \sqrt{R_{\min}}}{\sqrt{R_{\min}} - \sqrt{R_{\max}}} \tag{4}$$

The as obtained SiBCN ceramic sensor head and matching resistor were assembled by a stainless steel case with alumina plates on both sides of the sensor head for isolating purpose, as shown in Fig. 2. The inverse T-shaped stainless steel is used as an indenter to apply the extra pressure. A spring was used to insure the closed contact of electrodes and to fasten the sensor head.

The assembled SiBCN ceramic pressure sensor was tested at room temperature with the pressure up to 10 MPa. The overall sensor test setup was illustrated schematically in Fig. 3. The pressure sensor testing system

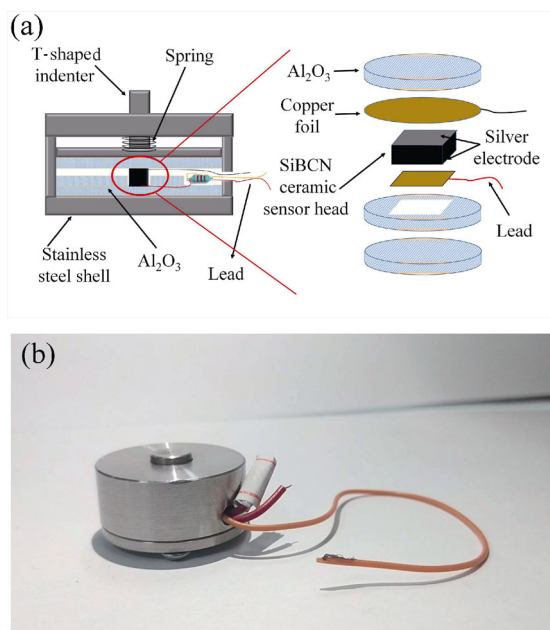


Fig. 2 SiBCN ceramic pressure sensor: (a) structure design and (b) assembled sensor.

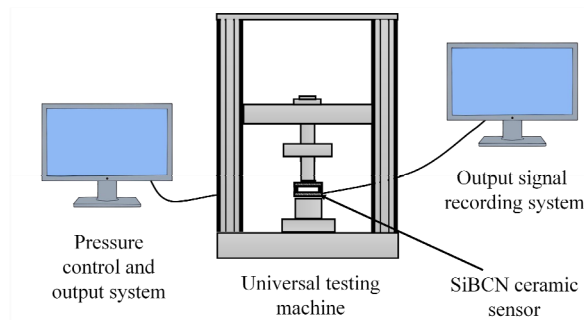


Fig. 3 Schematic drawn of SiBCN ceramic pressure sensor test setup.

mainly consists of three parts, namely, voltage regulator power supply, loading & control system, and output signal recording system. The excitation voltage of the regulated power supply is 9 V, at which the signal variation of pressure sensor can be well detected. The output pressure is provided by an electric universal testing machine with a pressure application rate of 0.5 mm/min (ZQ-990B, Zhiqu, Dongguan, Guangdong, China, equipped with a load cell of 500 N in the maximum). The output voltage signal was recorded by a digital multi-meter (VICTOR-86C, Victor Hi-Tech Co., Ltd., Shenzhen, China).

3 Results and discussion

3.1 Giant piezoresistivity of polymer-derived SiBCN ceramic

The pressure–resistance relationship of polymer-derived SiBCN ceramic is presented in Fig. 4. It can be seen that the resistance of SiBCN ceramic sensor head decreases monotonically with increasing applied pressure indicating that SiBCN ceramic is adequate for pressure sensing.

K defined as Eq. (5) is a crucial parameter to

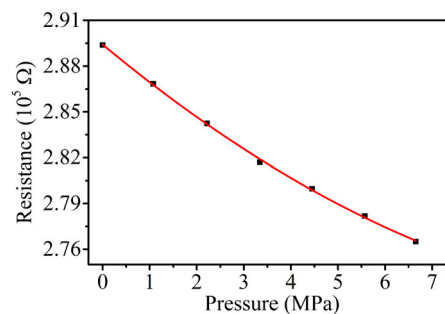


Fig. 4 Pressure–resistance relationship of SiBCN ceramic sensor head.

evaluate the resistance variation ability with applied pressure, which also reflects the sensitivity of a pressure sensor. The larger the K is, the higher sensitivity of the sensor is.

$$K = \frac{dR / R}{d\varepsilon} = E \frac{dR / R}{d\sigma} \tag{5}$$

where R is the resistance, σ is the applied stress, and E is the Young’s modulus of the material, which can be estimated by the following equation [31]:

$$E = E_0(1 - 1.9p + 0.9p^2) \tag{6}$$

where E_0 is Young’s modulus of fully dense SiBCN material (170 GPa) [20], and p is the porosity of the specimen measured to be ~23.7 vol%. Calculated from Eq. (6), the Young’s modulus of SiBCN ceramic sensor head studied here is ~102 GPa. Then, the relative K of SiBCN ceramic sensor head can be calculated using Eq. (5) and is shown in Fig. 5. Interestingly, the SiBCN ceramic exhibits an extremely high K up to 5500, due to the unique structure of PDCs [32,33], which is much higher than that of Si [11] and SiC [12] material, indicating that SiBCN ceramic is a promising material for pressure sensing application with high sensitivity.

3.2 SiBCN ceramic sensor performance

In order to fully investigate the performance of SiBCN ceramic pressure sensor, the feasibility, accuracy, repeatability, and stability were addressed systematically by using the testing platform shown in Fig. 3. The variation of output voltage as a function of the applied pressure was recorded in Fig. 6. The output voltage increases monotonously with the pressure increasing due to the outstanding piezoresistivity of SiBCN ceramics. The voltage–pressure curve shows a perfect linearity, which explores the great feasibility and reliability of SiBCN ceramic pressure sensor.

In order to verify the accuracy and response ability of SiBCN ceramic pressure sensor, the step loading–unloading experiment was considered, as shown in Fig. 7. The applied pressure increased steeply from 0 to 10 MPa with an interval of 1 MPa (black line in Fig. 7) and the output voltage shows a similar trend correspondingly, varies from 1.09 to 1.22 V. Meanwhile, the unloading cycle shows the same trend with the opposite direction. Specially, the output voltage increased synchronously even with the abrupt increasing of pressure at the top point of Fig. 7. The loading–unloading cycle reveals that the SiBCN ceramic sensor possesses excellent stability, accuracy, and fast response speed.

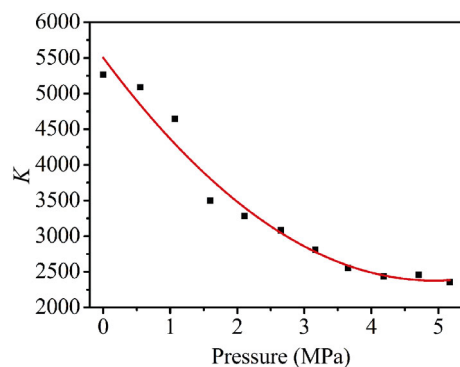


Fig. 5 K of SiBCN ceramic as a function of pressure.

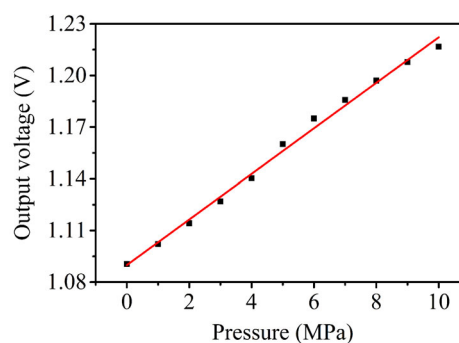


Fig. 6 Output voltage and pressure relationship of SiBCN ceramic pressure sensor.

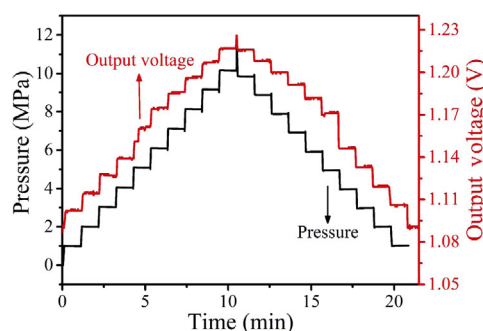


Fig. 7 Loading–unloading cycle of SiBCN ceramic pressure sensor.

To further evaluate the repeatability and stability of SiBCN ceramic sensor, the 50 cycles of loading–unloading test was carried out, as shown in Fig. 8. From the loading and unloading process (Fig. 8(a)), it can be concluded that the output voltage follows up pressure increase and/or decrease closely without any delay and obvious deviation, indicating that SiBCN ceramic sensor possesses excellent repeatability. The maximum and minimum output voltages of each cycle were plotted in Fig. 8(b). The maximum and minimum output voltages of each cycle remain constant, no obvious drift, meaning that the SiBCN ceramic sensor owns excellent stability.

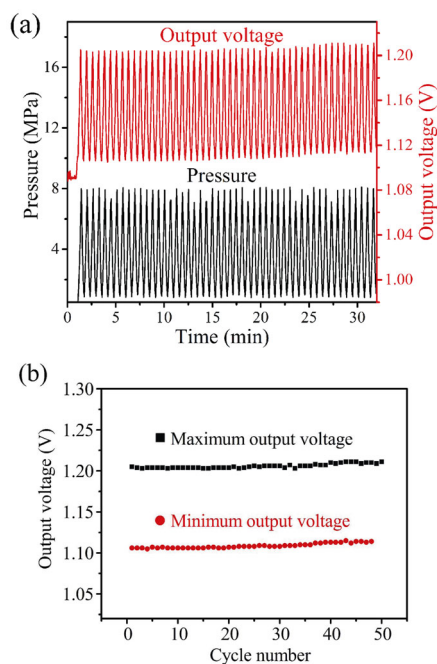


Fig. 8 Repeatability evaluation of SiBCN ceramic pressure sensor: (a) 50 loading–unloading cycles and (b) maximum and minimum output voltage of each cycle.

4 Conclusions

In this study, a piezoresistive pressure sensor with polymer-derived SiBCN ceramic as sensing material and stainless steel as frame is designed and tested. The polymer-derived SiBCN ceramic head exhibits a giant piezoresistivity of K as high as 5500, which insures a high sensitivity of the as designed pressure sensor. In addition, the SiBCN ceramic sensor exhibits excellent accuracy, repeatability, and stability in the pressure range of 0–10 MPa. Combining with the excellent high temperature thermo-mechanical properties, the polymer-derived SiBCN ceramic pressure sensor is very promising to be used at the high temperature and harsh environments.

Acknowledgements

The authors appreciate the financial support from the National Natural Science Foundation of China (No. U1904180) and Key Scientific Research Projects of High Education Institutions of Henan province (No. 19A430025).

References

- [1] Smith G. The application of microtechnology to sensors for

- the automotive industry. *Microelectron J* 1997, **28**: 371–379.
- [2] Prosser SJ. Advances in sensors for aerospace applications. *Sensor Actuat A: Phys* 1993, **37–38**: 128–134.
- [3] Tung TT, Robert C, Castro M, *et al.* Enhancing the sensitivity of graphene/polyurethane nanocomposite flexible piezoresistive pressure sensors with magnetite nano-spacers. *Carbon* 2016, **108**: 450–460.
- [4] Park SJ, Kim J, Chu M, *et al.* Flexible piezoresistive pressure sensor using wrinkled carbon nanotube thin films for human physiological signals. *Adv Mater Technol* 2018, **3**: 1700158.
- [5] Liu H, Dong MY, Huang WJ, *et al.* Lightweight conductive graphene/thermoplastic polyurethane foams with ultrahigh compressibility for piezoresistive sensing. *J Mater Chem C* 2017, **5**: 73–83.
- [6] Masheeb F, Stefanescu S, Ned AA, *et al.* Leadless sensor packaging for high temperature applications. In *Technical Digest. MEMS IEEE International Conference. Fifteenth IEEE International Conference on Micro Electro Mechanical Systems*. Las Vegas, NV, USA: IEEE, 2002: 392–395.
- [7] Li M, Tang HX, Roukes ML. Ultra-sensitive NEMS-based cantilevers for sensing, scanned probe and very high-frequency applications. *Nat Nanotech* 2007, **2**: 114–120.
- [8] Zaitsev AM, Burchard M, Meijer J, *et al.* Diamond pressure and temperature sensors for high-pressure high-temperature applications. *Phys Stat Sol (a)* 2001, **185**: 59–64.
- [9] Ned AA, Okojie RS, Kurtz AD. 6H-SiC pressure sensor operation at 600 °C. In *1998 Fourth International High Temperature Electronics Conference*. Albuquerque, NM, USA: IEEE, 1998: 257–260.
- [10] Kurtz AD, Ned AA. Hermetically sealed ultra high temperature silicon carbide pressure transducers and method for fabricating same. U.S. Patent 6058782, May 2000.
- [11] Kervran Y, de Sagazan O, Crand S, *et al.* Microcrystalline silicon: Strain gauge and sensor arrays on flexible substrate for the measurement of high deformations. *Sensor Actuat A: Phys* 2015, **236**: 273–280.
- [12] Phan HP, Dao DV, Tanner P, *et al.* Thickness dependence of the piezoresistive effect in p-type single crystalline 3C-SiC nanothin films. *J Mater Chem C* 2014, **2**: 7176–7179.
- [13] Riedel R, Kienzle A, Dressler W, *et al.* A silicoboron carbonitride ceramic stable to 2000 °C. *Nature* 1996, **382**: 796–798.
- [14] Wang YG, An LN, Fan Y, *et al.* Oxidation of polymer-derived SiAlCN ceramics. *J Am Ceram Soc* 2005, **88**: 3075–3080.
- [15] Wang YG, Fei WF, An LN. Oxidation/corrosion of polymer-derived SiAlCN ceramics in water vapor. *J Am Ceram Soc* 2006, **89**: 1079–1082.
- [16] Wang YG, Fei WF, Fan Y, *et al.* Silicoaluminum carbonitride ceramic resist to oxidation/corrosion in water vapor. *J Mater Res* 2006, **21**: 1625–1628.
- [17] Zhang LG, Wang YS, Wei Y, *et al.* A silicon carbonitride ceramic with anomalously high piezoresistivity. *J Am Ceram Soc* 2008, **91**: 1346–1349.
- [18] Li N, Cao YJ, Zhao R, *et al.* Polymer-derived SiAlOC

- ceramic pressure sensor with potential for high-temperature application. *Sensor Actuat A: Phys* 2017, **263**: 174–178.
- [19] Cao YJ, Yang XP, Zhao R, *et al.* Giant piezoresistivity in polymer-derived amorphous SiAlCO ceramics. *J Mater Sci* 2016, **51**: 5646–5650.
- [20] 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.
- [21] Fu SY, Zhu M, Zhu YF. Organosilicon polymer-derived ceramics: An overview. *J Adv Ceram* 2019, **8**: 457–478.
- [22] Zhao H, Chen LX, Luan XG, *et al.* Synthesis, pyrolysis of a novel liquid SiBCN ceramic precursor and its application in ceramic matrix composites. *J Eur Ceram Soc* 2017, **37**: 1321–1329.
- [23] Kong J, Wang MJ, Zou JH, *et al.* Soluble and meltable hyperbranched polyborosilazanes toward high-temperature stable SiBCN ceramics. *ACS Appl Mater Interfaces* 2015, **7**: 6733–6744.
- [24] Thiagarajan GB, Devasia R. Simple and low-cost synthetic route for SiBCN ceramic powder from a boron-modified cyclotrisilazane. *J Am Ceram Soc* 2019, **102**: 476–489.
- [25] Sarkar S, Gan ZH, An LN, *et al.* Structural evolution of polymer-derived amorphous SiBCN ceramics at high temperature. *J Phys Chem C* 2011, **115**: 24993–25000.
- [26] Liao N, Jia DC, Yang ZH, *et al.* Enhanced mechanical properties and thermal shock resistance of Si₂BC₃N ceramics with SiC coated MWCNTs. *J Adv Ceram* 2019, **8**: 121–132.
- [27] Kousaalya AB, Kumar R, Packirisamy S. Characterization of free carbon in the as-thermolized Si-B-C-N ceramic from a polyorganoborosilazane precursor. *J Adv Ceram* 2013, **2**: 325–332.
- [28] Chen YH, Yang XP, Cao YJ, *et al.* Effect of pyrolysis temperature on the electric conductivity of polymer-derived silicoboron carbonitride. *J Eur Ceram Soc* 2014, **34**: 2163–2167.
- [29] Ramakrishnan PA, Wang YT, Balzar D, *et al.* Silicoboron–carbonitride ceramics: A class of high-temperature, dopable electronic materials. *Appl Phys Lett* 2001, **78**: 3076–3078.
- [30] Ding Q, Ni DW, Wang Z, *et al.* 3D C_f/SiBCN composites prepared by an improved polymer infiltration and pyrolysis. *J Adv Ceram* 2018, **7**: 266–275.
- [31] Kingery WD, Bowen HK, Uhlmann DR. *Introduction to Ceramics*. New York, U.S.: John Wiley and Sons, 1976.
- [32] Wang YS, Zhang LG, Fan Y, *et al.* Stress-dependent piezoresistivity of tunneling-percolation systems. *J Mater Sci* 2009, **44**: 2814–2819.
- [33] Wang YG, Ding J, Feng W, *et al.* Effect of pyrolysis temperature on the piezoresistivity of polymer-derived ceramics. *J Am Ceram Soc* 2011, **94**: 359–362.

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/>.