Preparation and Properties of Pressureless-Sintered Porous Si_3N_4 Ceramics

Xiao Lin, Jinming Shi, Hongyu Gong, Yujun Zhang, Yurun Feng, Xue Guo, Bingying Xie, Yu Liu and Jiajun Wei

Abstract In this paper, the effect of benzoic acid on the porosity, dielectrical and mechanical properties of porous Si_3N_4 ceramics prepared by pressureless sintering was investigated. The results showed that the addition of benzoic acid improved the porosity and dielectrical properties of Si_3N_4 remarkably by pressureless sintering at 1700 °C for 60 min. The porosity of sample reached 40.79% with 50 wt% benzoic acid addition and the reflectivity of the sample reached −45 dB at around 12 GHz.

X. Lin · H. Gong (✉) · Y. Zhang · Y. Feng · X. Guo · B. Xie
Y. Liu · J. Wei
Key Laboratory for Liquid-Solid Structural Evolution & Processing of Materials of Ministry of Education, Shandong University, Jinan 250061, China
e-mail: hygong@sdu.edu.cn

X. Lin
e-mail: linxiao050994@sina.com

Y. Zhang
e-mail: yujunzhangcn@sdu.edu.cn

Y. Feng
e-mail: 765132878@qq.com

X. Guo
e-mail: 389702129@qq.com

B. Xie
e-mail: 1390830827@qq.com

Y. Liu
e-mail: 804512856@qq.com

J. Wei
e-mail: 1558724515@qq.com

X. Lin · H. Gong · Y. Zhang · Y. Feng · X. Guo · B. Xie · Y. Liu · J. Wei
Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Jinan 250061, China

J. Shi
College of Engineering, Peking University, Beijing 100871, China
e-mail: 413735337@qq.com

Y. Han (ed.), *Advanced Functional Materials*,
https://doi.org/10.1007/978-981-13-0110-0_12

Keywords Si_3N_4 · Pressureless sintering · Benzoic acid · Dielectric properties

Introduction

Si_3N_4 ceramics attract a lot of attentions for its outstanding properties such as low dielectric constant, high hardness, wear resistance, corrosion resistant and thermal-shock resistance under room temperatures and elevated temperatures [1, 2]. Porous Si_3N_4 ceramics combine the advantages of porous ceramics and Si_3N_4 ceramics with low density, high specific surface area, heat resistance, high fracture toughness and high strength [3]. Porous Si_3N_4 ceramics have great application potential in wave-transmitting materials and wave absorbing matrix [4–6] for its excellent dielectric properties, and the changeable dielectric constant. However, porous Si_3N_4 ceramics with good properties are hard to prepared successfully because of its porosity and high sintering temperature. We decided to use pore forming agent [7] and pressureless sintering to prepare porous Si_3N_4 ceramics, this access has simple process, great controllability and the convenience for large-scale production.

Zhang et al. [8] has prepared porous Si_3N_4 ceramics with high porosity and high strength by adding nano carbon powder as pore forming agent to Si_3N_4 matrix, whose porosity was over 40%, bending strength was more than 100 MPa with addition of 5 wt% carbon. Wang et al. [9] has synthesized BN/Si_3N_4 composite wave-transmitting ceramics by pressureless sintering with porosity 40.8%, dielectric constant and dielectric loss 4.0 and 3.3×10^{-3} respectively with addition of 5 wt% PMMA.

In this study, porous Si_3N_4 ceramics was prepared by pressureless sintering with α-Si_3N_4 powders, Y_2O_3 and Al_2O_3 as sintering aids and benzoic acid as pore forming. The effect of benzoic acid on the dielectrical and mechanical properties of porous Si_3N_4 ceramics was investigated.

Experimental Procedure

α-Si_3N_4 powder (0.5 μm particle size, purity >93%, Beijing Ziguang Co. PR China), Y_2O_3 (purity >99%, Hangzhou Wanjing Co. PR China), Al_2O_3 (purity >99%, Shanghai Macklin Co. PR China) and benzoic acid (purity >99%, Guoyao Co. PR China) were used as received. α-Si_3N_4 (90 wt%), Al_2O_3 (1.5 wt%), Y_2O_3 (8.5 wt%), PVP (1 wt%) and benzoic acid (0–50 wt%) were ball milled in ethanol for 15 min with Si_3N_4 balls as media. After milling, the mixed slurries were dried in a drying oven and then pass through a 60-mesh screen. The green specimens were formed by dry pressing and then removed pore forming agent under 200 °C. These porous compacts were sintered at 1700 °C for 60 min under a nitrogen atmosphere by pressureless sintering method.

We used X-Ray diffraction (XRD, D/max-RC) to identify the phase composition. The morphology and the microstructures were characterized by scanning electron microscope (SEM, JSM-6380LA). The porosity of the sintered body was calculated by the Archimedes' method. Dielectric constant and dielectric loss were tested through coaxial transmission reflection method (Agilent-N 5244A VNA), the band range is 2–18 GHz. Flexural strength and fracture toughness were measured by three-point bending test and SENB technique respectively.

Results and Discussion

Figure 1 shows the XRD spectra of porous Si_3N_4 ceramics by adding different contents of benzoic acid. The main crystal phases of all samples are β-Si_3N_4 phase and no α-Si_3N_4 phase, indicated that the crystalline phase transition of Si_3N_4 was complete during the sintering process, no matter what amount of pore forming add in the ceramics. Besides β-Si_3N_4, there is $Y_5Si_3O_{12}N$ in the specimen. It is due to Y–Si–Al–O liquid phase [10] was formed at around 1200 °C by the reaction with sintering aids and Si_3N_4 and SiO_2 on its surface, then α-Si_3N_4 separated out β-Si_3N_4 grain by dissolution precipitation. The liquid phase promoted the phase transition and densification process of Si_3N_4 at high temperatures, and the liquid phase finally crystallized into $Y_5Si_3O_{12}N$ phase.

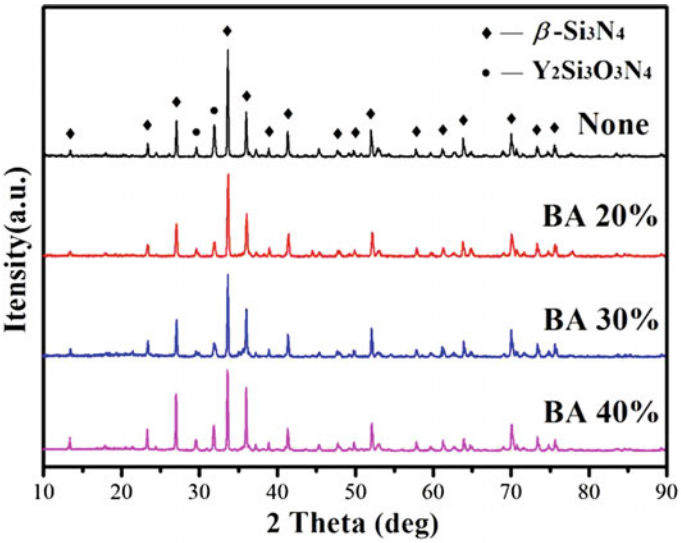


Fig. 1 XRD patterns of porous Si_3N_4 ceramics adding different contents of pore-forming agent (benzoic acid)

Figure 2 presents the SEM images of porous Si_3N_4 on fracture surfaces adding different contents of benzoic acid. We can see the equiaxed α-Si_3N_4 has been transformed into columnar β-Si_3N_4 during the sintering process. Figure 2a is Si_3N_4 without pore formers, so there are little pores inside and the grains are small and arranged closely. The benzoic acid initial particle size is small, the decomposition temperature is low, so the pore sizes are small, and shrinkage is large at high temperatures during the densification process. Therefore, the sintered body has closely spaced grains, small pore sizes and uniform distribution. As the BA content

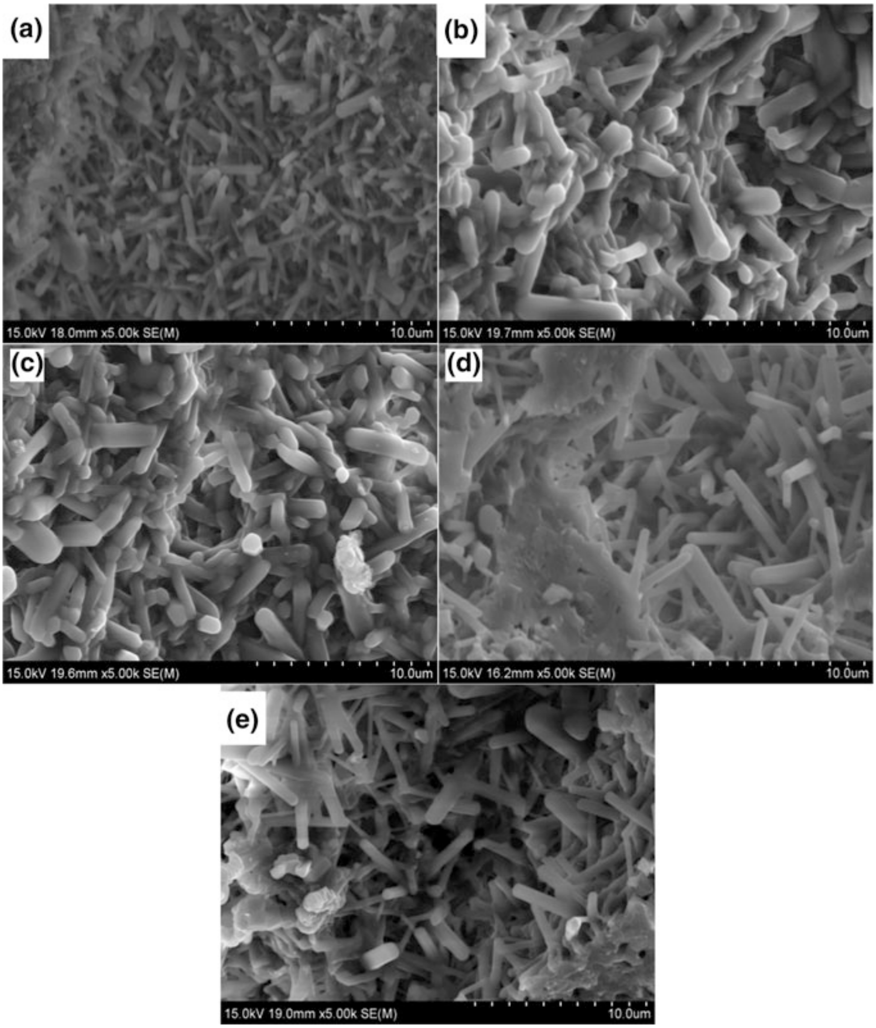


Fig. 2 SEM images of porous Si_3N_4 on fracture surfaces adding different contents of benzoic acid: **a** 0% **b** 20%; **c** 30%; **d** 40%; **e** 50%

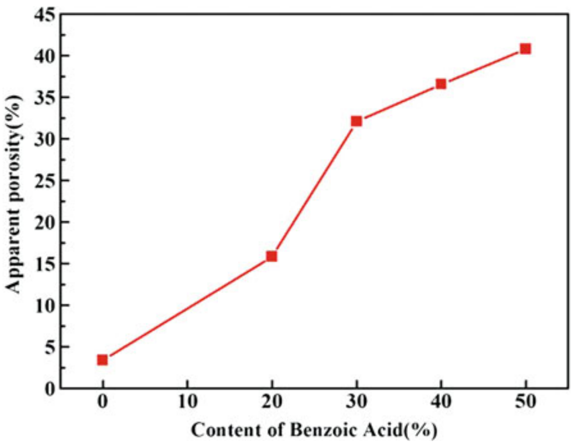
was increased from 20 to 50 wt%, the pores sizes and quantity in the samples was increased. But the addition amount has no obvious size or size distribution influence on pores of the porous Si_3N_4 ceramics. There are some grains bonded into block areas [11], it is because the amount of β-phase has limited the growth space among grains, restrained the growth of long columnar grains, then the grains become short and thick and bonded together.

The relationship between the content of benzoic acid and porosity of Si_3N_4 ceramics has been shown in Fig. 3. With the increase of pore addition agent mass fraction, the apparent porosity of materials increases, and the amplitude decreases, this is because pores arranged more closely, and it is more difficult to exclude. At the meantime, the pores will produce a certain shrinkage during the pressureless sintering process, and the rate of grain boundary movement will be faster with the increase of the number of pores, that is to say, the porosity will be reduced more and faster during the process, and the mechanical properties will be reduced too. The porosity of specimens reached 40.79% at most with 50 wt% benzoic acid added.

The dielectric properties of porous Si_3N_4 ceramics with different contents of benzoic acid has been presented in Fig. 4. The complex dielectric constant and dielectric loss are key parameters to characterize the dielectric properties of materials, the real part (dielectric constant) is relative to polarization, the imaginary part represents dielectric loss [12]. Although the high imaginary part means good microwave absorption performance, but too high values are unfavorable to impedance matching and may lead to strong reflection and weak absorption [13].

According to the previous analysis, the affecting factors on the dielectric properties of the sample are mostly porosity. From Fig. 4a, we can see the real permittivity is low in the specimen, and the value becomes lower with the porosity goes up except with the 40 wt% benzoic acid, it is probably because the block areas in the material. The reason for some negative dielectric loss values in the images is that the testing device is unstable at the beginning of the test. The sharp peaks in the

Fig. 3 Effect of adding different benzoic acid on apparent porosity of porous Si_3N_4 ceramics



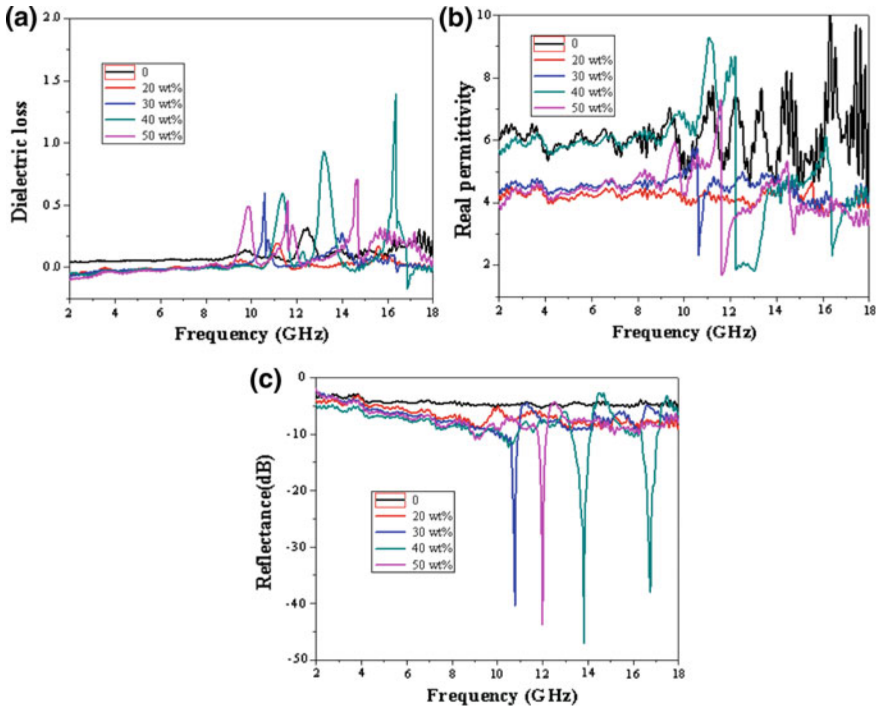


Fig. 4 Dielectric properties of porous Si_3N_4 ceramics with different contents of benzoic acid **a** real permittivity; **b** dielectric loss; **c** reflectance

picture are due to resonance absorption, and the position of the occurrence coincides with the location of the dielectric loss and reflectance peaks. The Si_3N_4 ceramics of 0 and 20 wt% benzoic acid have low dielectric loss, and there are almost no peak in the whole range. The peaks moves toward higher frequencies as the porosity increases. The reflectivity under −10 dB means the absorption rate of electromagnetic wave can reach more than 90% [14]. The reflectivity of the sample adding with 50 wt% benzoic acid can reach −45 dB at around 12 GHz, but the absorption band is not wide.

Figure 5 shows the mechanical properties of the specimens. The mechanical properties will declined with the porosity increased generally, because the presence of pores causes localized stress concentration and the reduced solid section, the actual stress increased and the strength decreased [15, 16]. The flexural strength is completely according with the law, the value is the lowest and the porosity of the samples is the highest when benzoic acid content is 50 wt%. However, the fracture toughness is a little improved as the porosity increased to 20 wt%, because the small pores with uniform dispersion are produced after pore forming agent is decomposed, maybe it can play a role of micro crack toughening and strengthen the toughness.

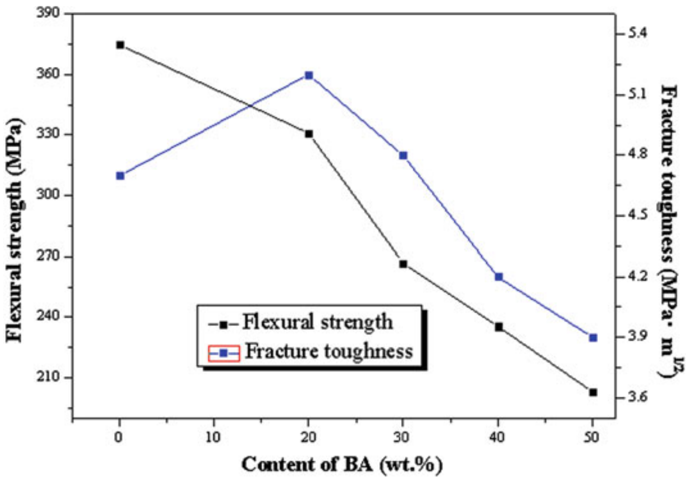


Fig. 5 Influence of the benzoic acid on the flexural strength and fracture toughness of porous Si_3N_4 ceramics

Conclusions

(1) The addition of benzoic acid improves the porosity and dielectrical properties of Si_3N_4 remarkably by pressureless sintering at 1700 °C for 60 min. The porosity of specimen reaches 40.79% with 50 wt% benzoic acid addition and the reflectivity of the sample can reach −45 dB at around 12 GHz, but the mechanical properties are reduced a little bit compared with Si_3N_4 ceramic without pore former.

(2) The specimen adding with 50 wt% benzoic acid has small and evenly distributed pores, the reflectivity of the sample is low and there are some resonance absorption peaks in the whole range, so it can be a good electromagnetic wave transmitting material if it is further improved.

Acknowledgements This work was supported by the Natural Science Foundation of China (51572154) and the Natural Science Foundation of Shandong Province (2015ZRE27348).

References

1. O.A. Lukianova, V.V. Sirota, Dielectric properties of silicon nitride ceramics produced by free sintering. Ceram. Int. **43** (2017)
2. X. Hou et al., Corrosion behavior of porous silicon nitride ceramics in different atmospheres. Ceram. Int. **43**(5), 4344–4352 (2017)
3. S. Shan, et al., Research progress of porous silicon nitride ceramics. Bull. Chin. Ceram. Soc. **28**(1), 138–142 (2009)
4. R. Raj, et al., Oxidation kinetics of an amorphous silicon carbonitride ceramic. J. Am. Ceram. Soc. **84**(8), 1803–1810 (2001)

5. X. Yang et al., Fabrication and properties of porous silicon nitride wave-transparent ceramics via gel-casting and pressureless sintering. Mater. Sci. Eng., A **663**, 174–180 (2016)
6. Q. Li, X. Yin, L. Feng, Dielectric properties of Si_3N_4–SiCN composite ceramics in X-band. Ceram. Int. **38**(7), 6015–6020 (2012)
7. P. Wang, et.al., Research progress in preparation methods of porous silicon nitride ceramics. Mater. Rev. (2014) (s2)
8. Yong Zhang et al., Study on preparation and high strength of porous silicon nitride ceramics. Rare Met. Mater. Eng. **33**(6), 655–658 (2004)
9. W. Dong, C. Wang, in *Effect of Pore Forming Agent Content on the Structure and Properties of Porous BN/*Si_3N_4 *Composite Ceramic*. National academic year of high tech ceramics (2012)
10. Gu Qiang et al., Phase transformation and microstructure of Si_3N_4 under high temperature and high pressure. Aeronaut. Manuf. Technol. **443**(23/24), 80–82 (2013)
11. Yu. Fangli et al., Effect of sintering additives and amount of β-Si_3N_4 on properties of porous silicon nitride ceramics. J. Synth. Cryst. **40**(3), 772–778 (2011)
12. X. Wang, in *Preparation and Microwave Absorbing Properties of SiCN Precursor Ceramics* (Shandong university, 2015)
13. R.C. Che et al., Microwave absorption enhancement and complex permittivity and permeability of Fe encapsulated within carbon nanotubes. Adv. Mater. **16**(5), 401–405 (2004)
14. L. Gao, X.H. Jin, J.G. Li et al., BN/Si_3N_4 nanocomposite with high strength and good machinability. Mater. Sci. Eng., A **415**(1), 145–148 (2006)
15. E. Rysyshkewitch, Compression strength of porous sintered alumina and zirconia[J]. J. Am. Ceram. Soc. **36**(2), 65–68 (1953)
16. S.J. Penn, N.M. Alford, A. Templeton et al., Effect of porosity and grain size on the microwave dielectric properties of sintered alumina. J. Am. Ceram. Soc. **80**(7), 1885–1888 (1997)