

Effect of BN content on microstructures, mechanical and dielectric properties of porous BN/Si₃N₄ composite ceramics prepared by gel casting

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Abstract

Porous BN/Si₃N₄ composite ceramics with different BN contents have been fabricated by gel casting. The rheological behaviors of the suspensions, microstructure, mechanical properties, dielectric properties and critical temperature difference of thermal shock (ΔT_C) of porous BN/Si₃N₄ composite ceramics with different BN contents were investigated. With BN contents increasing, the mechanical properties of the porous BN/Si₃N₄ composite ceramics were partially declined, but the dielectric properties and thermal shock resistances were enhanced at the same time. For the porous Si₃N₄ ceramic without BN addition, the porosity, flexural strength, dielectric constant and critical temperature difference were 48.1%, 128 MPa, 4.1 and 395 °C, while for the 10 vol% BN/Si₃N₄ porous composite ceramics, they were 49.4%, 106.6 MPa, 3.8, and 445 °C, respectively. The overall performance of the obtained porous BN/Si₃N₄ composite ceramics indicated that it could be one of the ideal candidates for high-temperature wave-transparent applications.

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1. Introduction

Silicon nitride (Si₃N₄) ceramics are one of the most promising wave-transparent materials due to their excellent properties such as high mechanical properties, good thermal shock resistance and moderate dielectric properties [1,2]. However, relatively high dielectric constant and dielectric loss tangent at elevated temperatures limit their applications in advanced aircrafts [3]. In addition, further utilization of Si₃N₄ ceramics has been restricted mainly due to the catastrophic fracture behavior for their brittle and hard nature. So the machinability of the as-sintered Si₃N₄ materials is extremely poor, especially for those components with complex shapes.

To improve the dielectric properties of Si₃N₄ ceramics at elevated temperatures, pores [4,5] or hexagonal boron nitride (h-BN) particles [6] were introduced as second-phase dispersion into the Si₃N₄ matrix. In recent years, based on the weak

boundary phase (WBP) concept [7], attempts have been made to develop various machinable ceramics by means of import WBP in matrices, and pores [8] or h-BN [9,10] was also regarded as a WBP. In BN/Si₃N₄ composite ceramics, the cleavage behavior of plate-like structured BN particles endowed the material with good machinability together with superior high thermal shock resistance [11]. Unfortunately, a remarkable decrease in fracture strength caused by the aggregation of BN particles has been observed when BN content in BN/Si₃N₄ composite increased to a certain level [12]. Therefore, the homogeneous dispersion of BN particles into the matrix is probably an effective way to ensure the mechanical properties of BN/Si₃N₄ composite ceramics. To achieve the above goals, hot pressing BN/Si₃N₄ ceramic nanocomposites have been fabricated by many researchers [9,13–15], and these nanocomposites exhibited improved mechanical properties. According to their researches, boric oxide/acid and organic reducing agent (urea) were used to prepare turbostratic BN (t-BN) powder or t-BN coating on α -Si₃N₄ particles. During subsequent sintering, t-BN converted into the thermodynamically stable h-BN, and then the

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homogeneous dispersion of BN particle in BN/Si₃N₄ nanocomposite was obtained. However, in order to prevent the loss of urea, this process requires excess urea and a small gas overpressure, making it difficult to control the stoichiometry of B and N source.

Gel casting is a near-net-shape technology and is well-established to fabricate homogeneous, complex-shaped and machinable green body with high green strength [16,17]. In the past decades, many researchers have demonstrated that gel casting was one of the most promising ways to increase the ceramic reliability and reduce the production costs [18–20]. Nevertheless, fabrication of BN/Si₃N₄ composites by gel casting and subsequently pressureless sintering has not yet been reported.

In our previous study, we had prepared porous silicon nitride ceramics by gel casting [21]. Based on that, in this article, we fabricated the porous BN/Si₃N₄ composite ceramics with homogeneous dispersion of BN particles by the gel casting technique. Effects of BN content on the rheological behaviors of the slurries were investigated, and the phase composition, microstructures, mechanical properties, dielectric properties and critical temperature shock difference of the porous BN/Si₃N₄ composite ceramics were discussed in details.

2. Experimental procedure

2.1. Materials processing

Si₃N₄ (α -phase > 93%, mean particle size 0.5 μ m) and h-BN (purity=99.5%, mean particle size 0.5 μ m) were employed as raw powders. 2 wt% La₂O₃ and 1 wt% Y₂O₃ (Aldrich Chemicals, purity=99.99%, particle size 50 nm) were used as sintering additives.

Aqueous slurries were prepared by mixing distilled water with a small amount (0.2 wt%) of ammonium salt of polyacrylic acid dispersant (99%, Tianjin Dengfeng Chemical Factory, Tianjin, China), and hydrochloric and ammonia were used to adjust the pH value to 8.5. Solid contents of the suspensions were fixed at 40 vol%, and different BN contents were added from 0 vol% to 15 vol%. Slurries were ball-milled with Si₃N₄ balls for 24 h in a plastic bottle.

Commercial agarose powder (99.8%, Beijing Aoboxing Bio-tech Co., Beijing, China) was used as gelation, and 3 wt% agarose aqueous solution were made as the method described by Santacruz et al. [22]. The agarose was introduced into the ceramic slurry by 0.5 wt% with regard to the powder mass. The suspension was degassed for 10 min before casting, then the resulting slurry was poured into a stainless steel mold (58 mm in diameter and 8 mm in height) which was pretreated at 60 °C, and subsequently cooled in a refrigerator with a temperature of about 2–5 °C. After solidification, the green bodies were demoulded and dried at room temperature under controlled humidity to avoid cracking and nonuniform shrinkage caused by rapid drying. After the samples were completely dried, organic matters were removed in a muffle furnace at 500 °C for 1 h in an air atmosphere with a heating

rate of 0.5 °C/min. Then, the samples were placed in a graphite crucible in a powder bed with a composition of 50 vol%:50 vol% for BN:Si₃N₄ and sintered in a graphite furnace at 1750 °C for 1 h under 0.1 MPa N₂ atmosphere.

2.2. Materials characterization

The rheological properties of ceramic suspensions were determined by a rotary rheometer (Model NSX-11A, Chengdu Instrument Factory, Chengdu, China). Porosity was determined by the Archimedes method using distilled water as a medium. Phase compositions were identified by X-ray diffraction (XRD, Rigaku, RINT-2000), using CuK α radiation at 40 KV and 100 mA. Morphologies were observed by scanning electron microscopy (SEM, FEI, Quanta-200). The thermal expansion coefficient of the obtained materials was determined by the thermal expansion instrument (NETZSCH DIL 402C). Samples were machined into standard bar samples of 36 mm \times 4 mm \times 3 mm and edges was beveled for three-point bending strength test, which was conducted on a mechanical testing machine (Shimadzu, AG-Is50) with a span of 30 mm at a crosshead speed of 0.5 mm/min, and five specimens were tested to obtain the average strength values. The fracture toughness was measured by a single edge notched beam (SENB) technique, the samples sizes were 20 mm \times 4 mm \times 2 mm, with a notch of 2 mm in depth and 0.2 mm in width. The fracture toughness testing was conducted by a three-point bending with a span of 15 mm and a crosshead speed of 0.05 mm/min. For the measurements of dielectric properties, specimens with a size of Φ 18 mm \times 1 mm were tested in the frequency range of 21–38 GHz at room temperature by RF impedance/material analyzer (Model 4291B, Agilent, USA).

3. Results and discussion

3.1. Rheological behavior of suspensions and machinable green body

The issue of how to fabricate high solid loading ceramic suspension with good rheological property is a crucial factor of gel casting; slurries with good fluidity lead to homogeneous dispersion of ceramic powders. Fig. 1 shows the influence of BN content on the viscosity of 40 vol% aqueous suspensions. As can be seen, the viscosity value at any given shear rate increased with increase in the content of BN, which meant that higher BN content was detrimental to get higher fluidity. In addition, all of the suspensions were characterized of shear-thinning behaviors due to the network that formed on the surface of ceramic particles by the dispersant concentration [23].

BN/Si₃N₄ suspension is a complex system in which many factors have significant effect on its rheological behaviors such as pH value, dispersant and its content, particle shape, solid content and so on. When pH value, dispersant and solid content were fixed, the particle shape became the key factor. Si₃N₄ raw material is equiaxed particle while BN has a

lamellar-type structure. The sketch map of Si_3N_4 powder in the dispersed medium with or without BN is shown in Fig. 2, there were two reasons for the decrease of slurry fluidity with BN addition. On the one hand, the specific surface area of flake BN was larger, so more water was needed to wet the particle surface when more BN were added. On the other hand, the equiaxed Si_3N_4 particles can pack denser than the flake BN, so more water was needed to fill the inter spaces between the ceramic particles when the BN content increases.

Compared to oxide ceramics, nitride ceramics have more complicated surface morphology which is detrimental to the aqueous dispersibility of nitride ceramic powders [24]. In addition, higher viscosity of the slurry when more BN was added may also attributed to the easy moisture absorption nature of B_2O_3 that presented in the surface of BN particles.

The dried green bodies prepared by aqueous gel casting have good machined performance. A macrograph of the 10 vol% BN/ Si_3N_4 green body is presented in Fig. 3. The sample has been machined by drilling, milling and sawing, which indicated that the green bodies have enough strength to take pre-processing.

3.2. Density of porous BN/ Si_3N_4 composite ceramics

Variations in the green density, sintering linear shrinkage and apparent porosity of the samples are shown in Table 1.

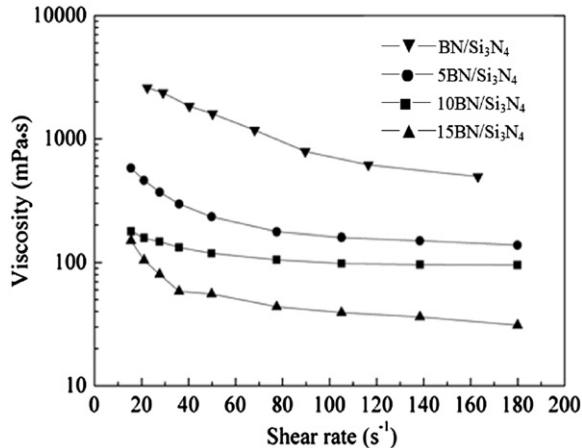


Fig. 1. Rheological behaviors of different suspensions with 40 vol% solids content.

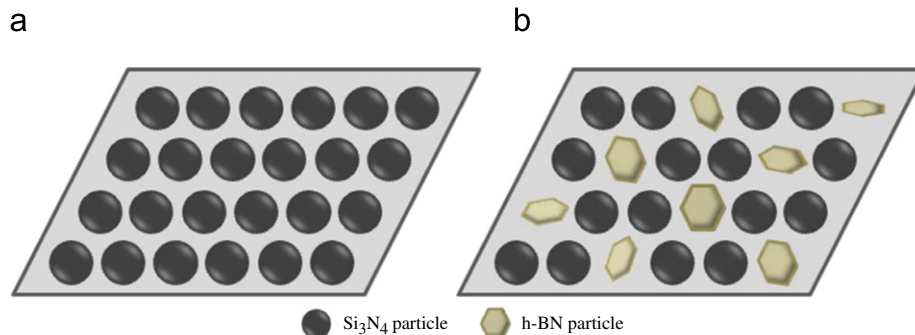


Fig. 2. Sketch map of the ceramic powders in dispersed medium, (a) without BN; (b) with BN.

The green density and sintering linear shrinkage decrease with the BN content increases, while the apparent porosity increases. The porosity was a combining result from green density and sintering shrinkage; increasing green density or shrinkage decreased the porosity. Moreover, it is well known that BN cannot be sintered in this work due to its relatively high sintering temperature, which led to the increasing of porosity in BN/ Si_3N_4 ceramics when more BN were added [7,9,14].

3.3. Phase compositions and microstructures of porous BN/ Si_3N_4 composite ceramics

Fig. 4 shows the XRD patterns of the obtained BN/ Si_3N_4 composite ceramics with different BN contents. It was revealed that $\beta\text{-Si}_3\text{N}_4$, $\alpha\text{-Si}_3\text{N}_4$ and BN were the dominate phases for all the four kinds of samples. La_2O_3 or Y_2O_3 was not detected in the XRD patterns, due to their amounts being too small to be detected. The diffraction intensity of BN enhanced with increasing BN amount, indicating that the BN did not participate in any reaction during the sintering process. According to the XRD patterns, the diffraction intensity of $\beta\text{-Si}_3\text{N}_4$ increased obviously with the increase in BN contents. The relative contents of $\beta\text{-Si}_3\text{N}_4$ and $\alpha\text{-Si}_3\text{N}_4$ were calculated according to the formula proposed by Hwang [25], by measuring the

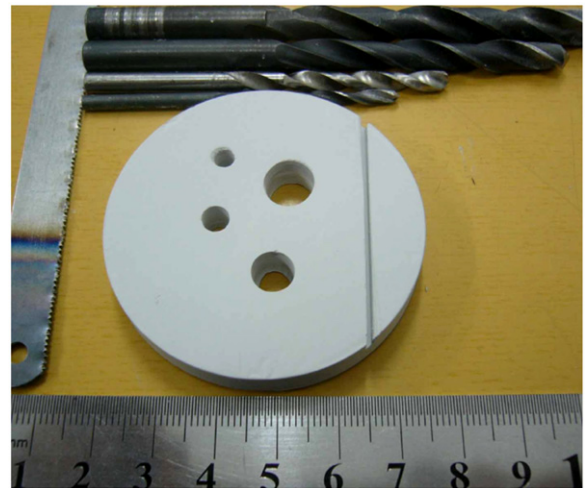


Fig. 3. Machinable BN/ Si_3N_4 green body containing 10 vol% BN.

Table 1
Green density, sintering linear shrinkage and porosity of the porous BN/Si₃N₄ composite ceramics.

Samples	Green density (vol%)	Sintering linear shrinkage (%)	Porosity (%)
Si ₃ N ₄	42.3	6.9	48.1
5BN/95Si ₃ N ₄	42.0	6.8	48.4
10BN/90Si ₃ N ₄	41.8	6.2	49.4
15BN/85Si ₃ N ₄	40.1	5.1	53.3

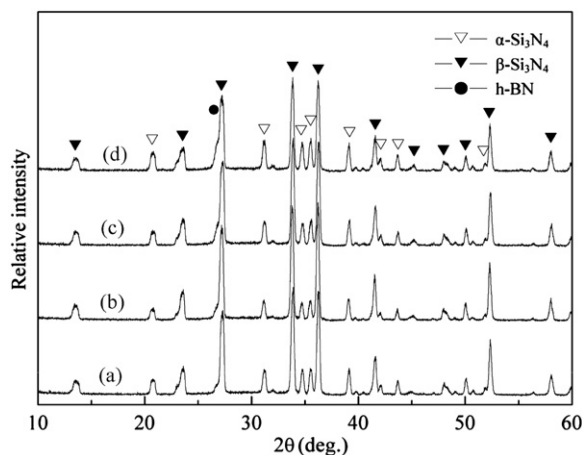


Fig. 4. XRD patterns of the porous BN/Si₃N₄ composite ceramics, (a) Si₃N₄, (b) 5BN/95Si₃N₄, (c) 10BN/90Si₃N₄ and (d) 15BN/85Si₃N₄.

Table 2
Relative content of α-Si₃N₄ and β-Si₃N₄ in porous BN/Si₃N₄ composite ceramics.

Sample codes	Relative content	
	α-Si ₃ N ₄ (%)	β-Si ₃ N ₄ (%)
Si ₃ N ₄	21.7	78.3
5BN/95Si ₃ N ₄	24.8	75.2
10BN/90Si ₃ N ₄	29.9	70.1
15BN/85Si ₃ N ₄	33.3	66.7

intensities of (101), (210) peaks of β-Si₃N₄ and the (102), (210) peaks of α-Si₃N₄:

$$\beta\% = \frac{I_{\beta(101)} + I_{\beta(210)}}{[I_{\alpha(102)} + I_{\alpha(210)}] + [I_{\beta(101)} + I_{\beta(210)}]} \quad (1)$$

where $I_{\alpha(102)}$ and $I_{\alpha(210)}$ denote the intensities of (102) and (210) diffraction planes of α-Si₃N₄, and $I_{\beta(101)}$ and $I_{\beta(210)}$ denote the intensities of (101) and (210) planes of β-Si₃N₄, respectively.

Table 2 shows the calculated results according to Fig. 4 and Eq. (1). BN content had a strong influence on the transformation of α- to β-Si₃N₄. For the sample of Si₃N₄ without BN addition, the relative content of β-Si₃N₄ was 78.3%, while for the sample with BN addition of 15 vol%, the relative content of β-Si₃N₄ decreased to 66.7%. Therefore, with increase in BN addition, the transformation of α- to β-Si₃N₄ was restrained.

The fracture surfaces of as-prepared samples observed by SEM are shown in Fig. 5. Compared with the conventional BN/Si₃N₄ composites which were prepared by dry processing [12], no large BN platelets or aggregates were found in Fig. 5(b) and all of the BN particles were well-distributed among the β-Si₃N₄ grains. This indicates that gel casting is a good way to fabricate composites with homogeneous dispersion of ceramic powders. However, as shown in Fig. 5(c) and (d), BN aggregates in the composites were detected and this phenomenon was more serious when BN content increased. From Figs. 5 and 1, we can get the conclusion that higher viscosity was detrimental to get homogeneously dispersion of BN. Therefore, good rheological property of the ceramic suspension was the prerequisite for fabricating high performance ceramic composites; otherwise, BN aggregates in BN/Si₃N₄ composites led to more and bigger defects in the ceramic microstructures.

From the SEM micrographs, the typically interlocked microstructure that elongated β-Si₃N₄ grains embedded in the small acicular one can also be detected. Formation of this microstructure can be explained by the anisotropic grain growth mechanism of β-Si₃N₄ grains [26]. In addition, observation of Fig. 5(a)–(d) indicated that the diameter and aspect ratio of the rod-like β-Si₃N₄ grains in composites decreased with the increase in BN content, which suggested that the growth of β-Si₃N₄ was restrained by BN. During the microstructure evolution stage of the sintering process, β-Si₃N₄ nucleus were first developed, then, the growth of β-Si₃N₄ grains would be inhibited when the β-Si₃N₄ nucleus met the BN particles in the growth direction during the grain growth stage. Thus the sample containing 5 vol% BN showed a more uniform microstructure than the one containing 15 vol% BN.

3.4. Mechanical properties of porous BN/Si₃N₄ composite ceramics

Mechanical properties of the composites are closely related to the phase compositions, porosities and microstructures. Fig. 6 shows the mechanical properties of the ceramics as-prepared as a function of BN content.

As expected, the flexural strength and fracture toughness of the ceramics all decreased monotonously with increasing BN content. Since BN was a relatively weak phase and the bonds between BN and Si₃N₄ were weaker than those between Si₃N₄ grains. When samples were bended, less energy was required for crack propagation with the increase of BN [7,13,15]. When more BN particles were incorporated, more flaws were introduced, and mechanical properties of the composites were deteriorated undoubtedly. Pores were also regarded as a WBP and the influence of porosity on the mechanical properties of BN/Si₃N₄ composites can be explained by the same theories mentioned above.

The changes of the mechanical properties for the composites are also related to their microstructures. The interlocking microstructure formed by rod-like β-Si₃N₄ grains was in favor of enhancing the flexural strength of

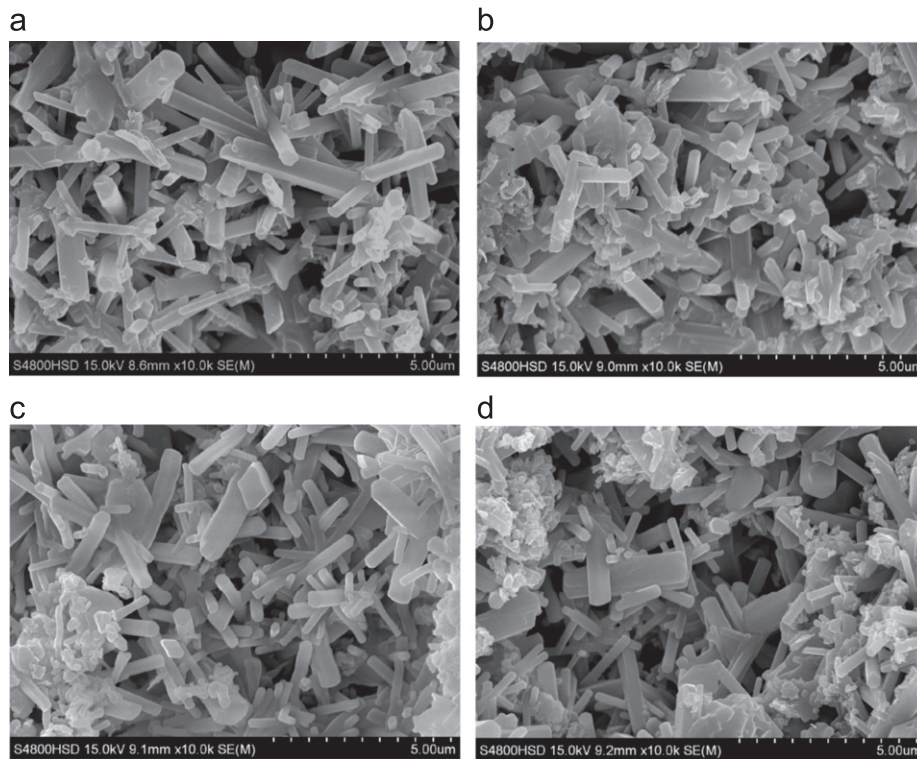


Fig. 5. Fractured surface morphologies of the porous BN/Si₃N₄ composite ceramics, (a) Si₃N₄, (b) 5BN/95Si₃N₄, (c) 10BN/90Si₃N₄ and (d) 15BN/85Si₃N₄.

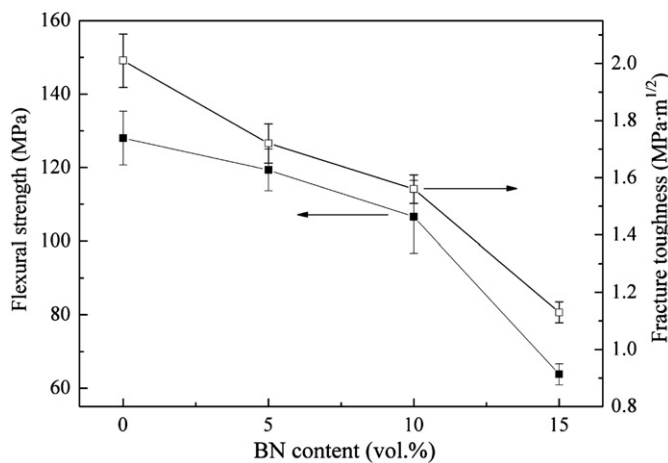


Fig. 6. Effect of BN content on the flexural strength and fracture toughness of the porous BN/Si₃N₄ composite ceramics.

BN/Si₃N₄ composites by the pull-out and bridging effect. However, BN agglomerates and porosity increased with increasing BN content, and these WBPs became the fracture sources which can severely decrease the composites' mechanical properties. In addition, according to Fig. 6, the deterioration of flexural strength and fracture toughness was moderate when BN content increased from 0 vol% to 10 vol%, but was seriously degraded when BN content up to 15 vol%. As indicated in Fig. 5, samples containing 5 vol% and 10 vol% BN both showed a more

uniform sizes of β -Si₃N₄ grains and homogeneous distribution of BN than the one with 15 vol%, and the composites composed of 15 vol% BN showed severe agglomeration of BN, which should be responsible for the rapid decrease of mechanical properties.

3.5. Dielectric properties of porous BN/Si₃N₄ composite ceramics

The dielectric properties of porous BN/Si₃N₄ composite ceramics strongly depend on their porosity, phase components. Effects of these factors on dielectric properties could be characterized by the mixture law. Compared to Si₃N₄, BN has excellent dielectric properties, and dielectric constant (ϵ) and dielectric loss tangent ($\tan \delta$) of pores can be regarded as 1 and 0, separately. Therefore, BN and pores have the role in decreasing the dielectric constant and dielectric loss tangent. Fig. 7 shows the variations of dielectric constant and dielectric loss tangent versus BN content in the frequency range of 21–33 GHz. The results show that the ϵ and $\tan \delta$ of BN/Si₃N₄ composite ceramics decreased obviously with the increasing of porosity and BN content, which fit well with the mixture law.

3.6. Critical temperature difference of thermal shock of porous BN/Si₃N₄ composite ceramics

Thermal shock resistance of ceramics is an important performance parameter for their applications. According to

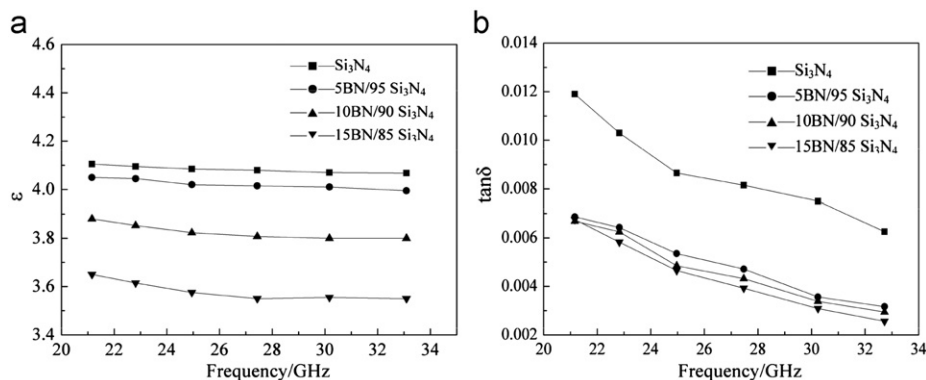


Fig. 7. Effect of BN content on the dielectric properties of the porous BN/Si₃N₄ composite ceramics, (a) dielectric constant and (b) dielectric loss tangent.

Table 3

Thermal expansion coefficient and the calculated values of the critical temperature difference of thermal shock of the porous BN/Si₃N₄ composite ceramics.

Samples	Thermal expansion coefficient (10 ^{−6} K ^{−1})	Critical temperature difference (°C)
Si ₃ N ₄	3.87	395.8
5BN/95Si ₃ N ₄	3.69	414.7
10BN/90Si ₃ N ₄	3.46	445.3
15BN/85Si ₃ N ₄	3.45	449.6

Fig. 6, the decrease of flexural strength and Young's modulus were asynchronous, so the introduction of BN may contribute to an excellent thermal shock property of the porous BN/Si₃N₄ composite ceramics. In order to evaluate the thermal stress crack initiation of ceramic materials, thermal stress fracture resistance parameter R , which is also known as critical temperature difference of thermal shock (ΔT_C) was introduced by Kingery [27] to estimate thermal stress fracture resistance of material:

$$R = \Delta T_C = \frac{\sigma_f(1-\nu)}{\alpha E} \quad (2)$$

where σ_f is the flexural strength, ν is the Poisson ratio (suppose to be 0.26 for all the samples [28]), E is the Young modulus, α is the coefficient of thermal expansion. Table 3 shows the Young modulus and thermal expansion coefficient from room temperature to 1200 °C, the calculated critical temperature differences of the thermal shock of the obtained samples based on Eq. (2) are also listed in Table 3.

According to Table 3, the calculated value increased with increase of BN content, which implied that a higher critical temperature difference was achieved through the addition of BN. The enhanced thermal shock resistance of the BN/Si₃N₄ composite ceramics with increasing BN content could be explained by two reasons. Firstly, as is known, BN has lower Young's modulus and thermal expansion coefficient compared to Si₃N₄. According to the mechanical properties of porous BN/Si₃N₄ composites, since the homogeneous dispersion of BN in Si₃N₄ matrix, flexural strength was less decreased as BN content increased from 0 vol% to 10 vol%.

Thus, enhanced ΔT_C was got based on Eq. (2). Secondly, the thermal shock resistance of ceramics could be improved greatly due to the porosity [29], since the pores distributed in composites could act as crack stoppers.

4. Conclusions

In this study, porous Si₃N₄ based ceramics with different volume fractions BN from 0 vol% to 15 vol% have been fabricated by the gel casting technique, and the dried green bodies with porosity from 48.1% to 53.3% had enough strength to take pre-processing. Due to the flake structure of BN, it has strong influence on the rheological behaviors of the suspensions. When BN content reached to 15 vol%, the viscosity increased dramatically to more than 1000 mpa s, which was detrimental to gel casting processing. Microstructure analysis revealed that BN particles can scatter uniformly in the interlocked microstructure formed by β -Si₃N₄ grains when BN content was less than 10 vol%. So we can get porous BN/Si₃N₄ composite ceramics with excellent performances of mechanical properties, dielectric properties and thermal shock resistance when the BN content was within this range. The overall performance of the obtained porous BN/Si₃N₄ composite ceramic is quite fit for the high-temperature wave-transparent applications.

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