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Short communication

Dielectric and mechanical properties of porous Si_3N_4 ceramics prepared via low temperature sintering

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Abstract

Borophosphosilicate bonded porous silicon nitride (Si_3N_4) ceramics were fabricated in air using a conventional ceramic process. The porous Si_3N_4 ceramics sintered at 1000–1200 °C shows a relatively high flexural strength and good dielectric properties. The influence of the sintering temperature and contents of additives on the flexural strength and dielectric properties of porous Si_3N_4 ceramics were investigated. Porous Si_3N_4 ceramics with a porosity of 30–55%, flexural strength of 40–130 MPa, as well as low dielectric constant of 3.5–4.6 were obtained.

Keywords: Porous Si_3N_4 ceramics; Dielectric constant; Borophosphosilicate; Low temperature sintering

1. Introduction

Radome materials for harsh working conditions demand a series of critical properties, such as low dielectric constant, high mechanical strength, excellent thermal shock resistance and rain erosion resistance [1]. Nowadays, silicon ceramics are mainly used as materials for radome and antenna windows owing to their excellent dielectric properties (dielectric constant ~3.5) [2]. However, their poor strength (usually less than 80 MPa) [3] and rain erosion resistance are not adequate for high speed vehicles.

Silicon nitride (Si_3N_4) ceramics have many superior properties, such as high-temperature strength, good oxidation resistance, thermal–chemical corrosion resistance, thermal shock resistance, low thermal expansion coefficient and good dielectric property [4–6]. The dielectric constant (ε) of α-Si_3N_4 is 5.6 and β-Si_3N_4 is 7.9 at room temperature, respectively. However, the dielectric constant of Si_3N_4 is still high for practical application. Pore design is generally believed as an effective way to decrease the dielectric constant of materials, but pores can also deteriorate the mechanical properties of ceramic materials. Therefore, it is important to keep dielectric and mechanical properties balanced to meet the practical application. Porous Si_3N_4 ceramics can be prepared in different ways, such as, adding fugitive substance [7], freeze drying [8], carbothermal nitridation [9], combustion synthesis [10], *in situ* reaction bonding [1], etc. As a covalent solid, Si_3N_4 is difficult to densify without a sintering additive. Usually, metal oxides ($Y_2O_3 + Al_2O_3$ [11], Er_2O_3 [12], Yb_2O_3 [13]) additives are required to get dense Si_3N_4 ceramics through liquid-phase sintering. However, the sintering temperature is still high. In order to obtain Si_3N_4 ceramics at low temperature, low temperature liquid phases, such as SiP_2O_7 [14], MgO-Al_2O_3-SiO_2 system [15], SiO_2 [16], borophosphosilicate (SiO_2-B_2O_3-P_2O_5) [17], etc., are used.

In this work, borophosphosilicate glass was used as sintering additive to prepare porous Si_3N_4 ceramics. The sintering behavior and the effect of additives on the porosity, flexural strength and dielectric constants of specimens were investigated.

2. Experimental procedure

α-Si_3N_4 (SN-E10, purity > 99.5%, α ratio > 95%, average particle size 0.5 μm; UBE Industries, Ltd., Tokyo, Japan), H_3PO_4 (purity ≥ 85 wt.%; Lingfeng company, Shanghai, China) and H_3BO_3 (purity ≥ 99.5 wt.%; Sino-pharm Chemical Reagent Co., SCRC; Shanghai, China), Ultra-fine SiO_2 (30 nm, Jialian Chemical Engineering Co. Ltd., Nanping, China) were used as the starting materials. For the preparation

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of borophosphosilicate glass, a mixture of H_3PO_4, H_3BO_3 and SiO_2 in the weight ratio of 1.77:1.38:4 was calcinated at 500 °C with heating and cooling rates of 2 °C/min with held for 2 h. With regard to the porous Si_3N_4 ceramics preparation, a mixture of α-Si_3N_4, H_3PO_4 and H_3BO_3 was ball-milled in water for 24 h; SiO_2 is the oxidization of Si_3N_4 during sintering. After being dried and sieved through a 100-mesh (154 μm) screen, the powder was pressed into rectangular bars with dimensions of 4.5 mm × 10.0 mm × 50.0 mm, the bars were then cold isostatically pressed at 200 MPa. The bars were firstly heated in air at 500 °C with heating rate of 2 °C/min and held for 2 h to prevent the pore expansion resulting from the volatilization of H_3PO_4 and H_3BO_3, then sintered at 1000–1200 °C with heating and cooling rates of 5 °C/min and held for 2 h in air atmosphere.

Differential thermal analysis (DTA) and thermogravimetry (TG) were performed using STA-429 (Netzsch, Germany) differential thermal analyzer with a speed of 10 °C/min in air. Specimens were machined into a rectangle bar with dimensions of 3.0 mm × 4.0 mm × 36.0 mm to measure the flexural strength via the three point bending test (Model AUTOGRAPH AG-I, Shimadzu, Japan), the support distance of 30.0 mm and a cross-head speed of 0.5 mm/min were used. The open porosity and bulk density were determined by the Archimedes method using distilled water as medium. Phase analysis was conducted by X-ray diffraction (XRD) via a computer-controlled diffractometer (Model RAX-10, Rigaku, Japan) with Cu Kα radiation (wavelength of 1.5418 Å). Morphology of porous Si_3N_4 ceramics was observed by scanning electron microscopy (SEM) (Model JXA-8100, JEOL, Tokyo, Japan). The complex permittivities of the specimens with the size of Ø 20.0 mm × 1.1 mm were measured in the frequency range of 100 MHz to 1 GHz at room temperature by RF impedance/material analyzer (Model 4291B, Agilent, USA)

3. Results and discussion

3.1. Characterization of borophosphosilicate glass

H_3PO_4 can react with H_3BO_3 at ∼100 °C as follows [14]:

$$H_3PO_4 + H_3BO_3 = BPO_4 + 3H_2O \quad (1)$$

The crystal structure of BPO_4 contains BO_4 and PO_4 tetrahedron. Meanwhile, BPO_4 is a copolymer of two water soluble and low melting oxides: boric oxide and phosphorous oxide. BPO_4 is a chemical inert glass with a good dielectric property ($\varepsilon \approx 4$) [17]. Thus, it is appropriate to use BPO_4 as the sintering additive in Si_3N_4 preparation. Moreover, the strength of Si_3N_4 ceramics can be considerably improved by the addition of BPO_4 [18].

Fig. 1 shows the XRD pattern of the borophosphosilicate glass. The pattern can be indexed to two phases: BPO_4 and B_2O_3. B_2O_3 is derived from excessive H_3BO_3, which is also beneficial for decreasing sintering temperature. Fig. 2 shows the TG/DTA curves for the mixture of H_3PO_4, H_3BO_3 and SiO_2. The curves can be divided into two regions. From 70 °C to 180 °C, a sharp endothermic peak is observed and the weight loss is about 20 wt.%, corresponding to the formation of BPO_4 and evaporation of H_2O. Above 180 °C, the obvious weight loss is not observed in the TG, the DTA curve shows a wide peak owing to the crystallization of BPO_4, which was also reported by R. Hsu [19].

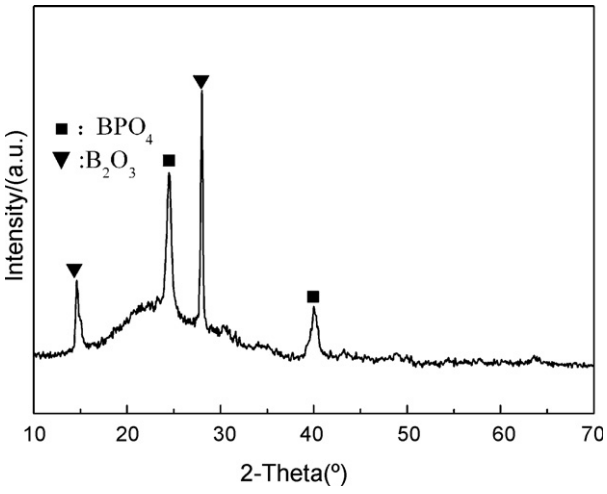

Fig. 1. XRD pattern of borophosphosilicate in the mass ratio of $H_3BO_3/H_3PO_4/SiO_2$ = 1.77:1.38:4 sintered at 500 °C for 2 h.

3.2. Phase and microstructure analysis of porous Si_3N_4 ceramics

Fig. 3 shows the XRD patterns of Si_3N_4 raw powder and porous Si_3N_4 ceramics. Compared to the pattern of raw Si_3N_4 powder, the weak peaks of BPO_4 and cristobalite (SiO_2) are found in the sintered Si_3N_4 ceramics. The relatively low content of BPO_4 indicates that the borophosphosilicate glass is amorphous, and the little amount of cristobalite (SiO_2) results from partial oxidation of Si_3N_4 in air [20].

Fig. 4 shows the relationship between sintering temperature and porosities of Si_3N_4 ceramics. The content of additives has

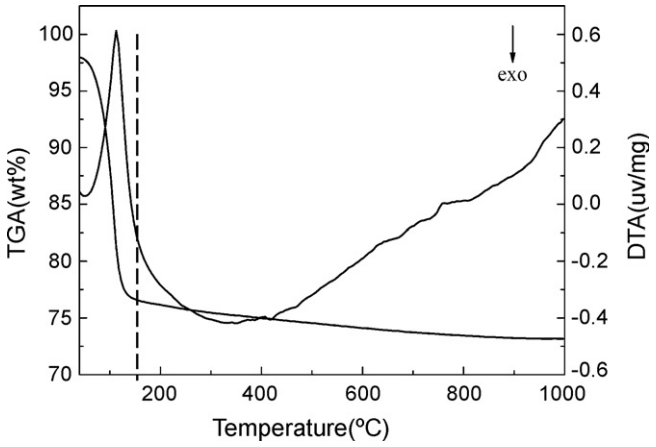

Fig. 2. Thermogravimetry (TG)-differential thermal analysis (DTA) curves of borophosphosilicate in the mass ratio of $H_3BO_3/H_3PO_4/SiO_2$ = 1.77:1.38:4.

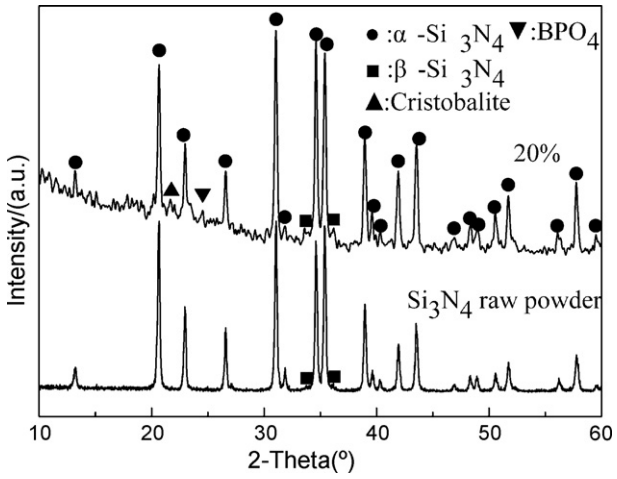

Fig. 3. XRD pattern of Si_3N_4 raw powders and ($H_3BO_3 + H_3PO_4$) bonded silicon nitride (Si_3N_4) ceramic sintered at 1150 °C for2 h.

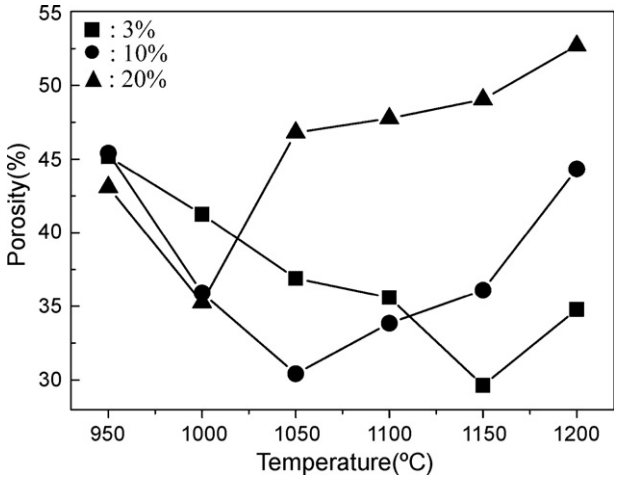

Fig. 4. Relationship between sintering temperature and porosities of Si_3N_4 ceramics with different contents of additives.

great effect on the porosity of porous Si_3N_4 ceramics. When the sintering temperature is below 1000 °C, the borophosphosilicate glass is helpful for Si_3N_4 densification during sintering process. The porosity of Si_3N_4 decreases with the increase in the content of borophosphosilicate glass. When the sintering temperature is above 1100 °C, the samples with more borophosphosilicate glass have higher porosity due to the evaporation of borophosphosilicate glass. On the other hand, with increasing sintering temperature, the porosity decreases first and then increases. For example, the porosity of specimen with 10% additives is 46–32% with the sintering temperature from 950 °C to 1050 °C, but when the sintering temperature is increased to 1200 °C, the porosity is 43%. This phenomenon is quite consistent with the glass properties, which is in favor of sintering process at low temperature instead of high sintering temperature owing to glass volatilization.

Fig. 5 shows the SEM images of the Si_3N_4 ceramics. The SEM micrographs indicate that both glass and sintering temperature have great effects on the microstructure of the porous Si_3N_4. The Si_3N_4 sintering processing is very complex, which is related to the glass evaporation, Si_3N_4 oxidation and oxidized-derived SiO_2 reaction with additives. Therefore, the

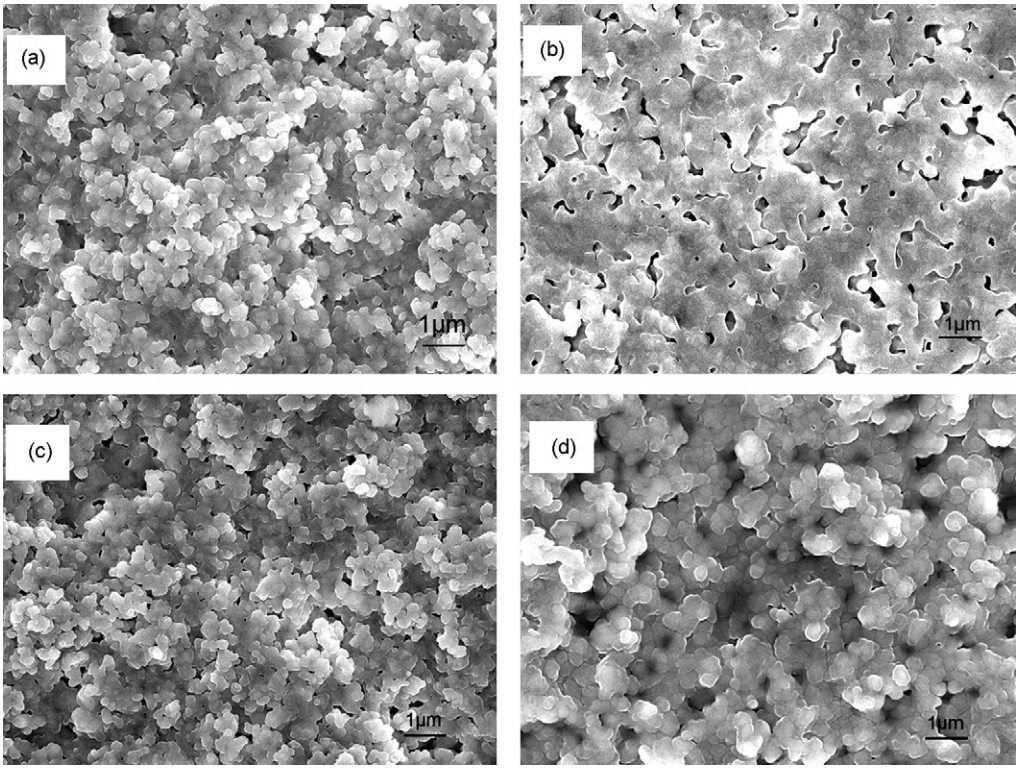

Fig. 5. Microstructure of porous silicon nitride (Si_3N_4) at different sintering temperatures with different contents of additives: (a) 1050 °C, 3 wt.%; (b) 1150, 3 wt.%; (c) 1150 °C, 10 wt%; (d) 1150 °C, 20 wt.%.

different sintering temperatures and the different contents of additives result in the different microstructure.

3.3. Mechanical and dielectric properties of porous Si_3N_4 ceramics

Generally, the flexural strength of porous ceramics is mainly dependent on porosity. The strength (σ) of porous ceramics is expressed as in the following equation [21,22]:

$$\sigma = \sigma_0 \exp(-\beta P) \quad (2)$$

where σ_0 is the strength at a porosity of 0, β is the structural factor, and P is the porosity. Fig. 6 shows the flexural strength of the sintered porous Si_3N_4 ceramics. The flexural strength is in the range of 30–130 MPa. The maximal flexural strength is 130 MPa when the sintering temperature is 1150 °C and the content of additive is 3 wt.%. More additives result in the improvement of flexural strength of Si_3N_4 at lower sintering temperature. However, more additives lead to decrease in flexural strength at higher temperature because of borophosphosilicate glass volatilization. The flexural strength increases firstly and then decreases, which is consistent with the result of Fig. 4. As shown in Fig. 6(b), the porosity of Si_3N_4 dominates the mechanical strength as expected from Eq. (2). Meanwhile, the flexural strength is affected by cristobalite (SiO_2) oxidized-derived from Si_3N_4. The cristobalite formed in Si_3N_4 oxidation is harmful for the strength of specimens, if the volume of cristobalite is larger than 12 vol% of specimen, which will have cracks [23].

According to the mixture rule, the dielectric constant of the two-phase composite is calculated as follows [24]:

$$\varepsilon = V_1\varepsilon_1 + V_2\varepsilon_2 \quad (3)$$

where ε is the dielectric constant of the composite, V_1 and V_2 are the volume fractions of phase 1 and phase 2, respectively; ε_1 and ε_2 are the dielectric constants of the phases. The variation of ε with porosity can be considered by using an approximation if the phase 2 is porosity ($\varepsilon = 1$). Eq. (3) reduces to

$$\varepsilon = \varepsilon_0 - P(\varepsilon_0 - 1) \quad (4)$$

where ε_0 is the dielectric constant of phase 1, and the fractional porosity is P [25]. It can be seen from Eq. (4) that the dielectric constant of porous ceramic decreases with increase in porosity.

Fig. 7 shows the relationship between the dielectric constant (ε) of the specimens and frequency. The dielectric constant of porous Si_3N_4 is influenced by the porosity, Si_3N_4, as well as the second phase, which consists of borophosphosilicate glass and cristobalite. Fig. 7(a) and (b) indicates that for the specimens with 3% additives, the higher sintering temperature results in higher dielectric constants, owing to the porosity having more effects than that of the oxidized-derived cristobalite. It can be seen from Eq. (3) that the constant of composite decreases more when the porosity ($\varepsilon \approx 1$) and the content of cristobalite ($\varepsilon \approx 3.5$) increase in the same magnitude. The dielectric constants of the specimens with 3%, 10%, and 20% additives are also shown in Fig. 7(b)–(d). The dielectric constant does not have great variation with increasing frequency. For 20% additive, namely curve in Fig. 7(d), the increase in porosity and borophosphosilicate glass result in the decrease in dielectric constants. However, the dielectric constant of curve in Fig. 7(c) is higher than that of the curve in Fig. 7(a) although it contains more borophosphosilicate glass, due to lower porosity. So porosity is the dominating factor for the dielectric constant of porous ceramics.

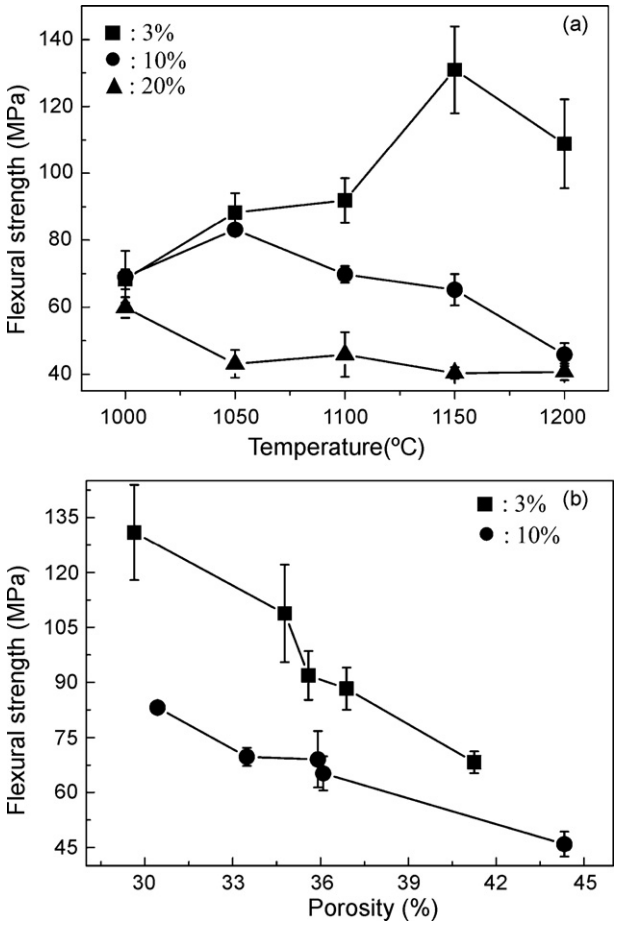

Fig. 6. Flexural strength of porous silicon nitride ceramics (Si_3N_4) with (a) different contents of additives at different sintering temperatures, (b) different porosities.

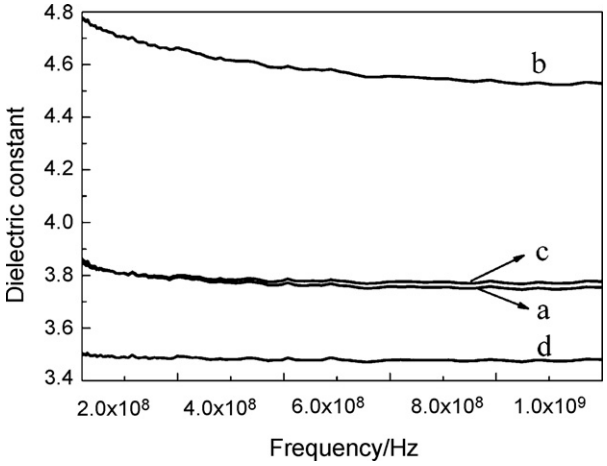

Fig. 7. Dielectric constant (ε) of porous silicon nitride (Si_3N_4) at different sintering temperatures with different contents of additives: (a) 1000 °C, 3 wt.%; (b) 1100 °C, 3 wt.%; (c) 1100 °C, 10 wt.%; (d) 1100 °C, 20 wt%.

4. Conclusions

Porous silicon nitride ceramics were fabricated at low temperature in air, using H_3BO_3 and H_3PO_4 as sintering additives. By changing the contents of additives and sintering temperature, porous Si_3N_4 ceramics with flexural strength of 30–130 MPa, porosity of 30–55% and dielectric constants of 3.5–4.6 can be obtained.

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