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Short communication

Mechanical and dielectric properties of porous Si_3N_4 ceramics using PMMA as pore former

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Abstract

Porous Si_3N_4 ceramics were prepared using PMMA as pore former, and the mechanical and dielectric properties were investigated, as a function of porosity. Higher porosity was achieved at lower sintering temperature with lower sintering additive and more PMMA. The flexural strength decreased exponentially with increasing the porosity and the pore size. The dielectric constant decreased with increasing the porosity and the frequency has less effect on the dielectric constant.

Keywords: B. Porosity; C. Mechanical properties; C. Dielectric properties; Porous Si_3N_4

1. Introduction

Silicon nitride (Si_3N_4) ceramics usually is described as an ideal engineering material because of its superior properties, such as the high-decomposition temperature, the high strength at room and elevated temperatures, low coefficient of friction and resistance to environments [1,2], as well as the excellent oxidation and thermal shock resistance [3–9]. Moreover, silicon nitride also has good dielectric properties and it attracts much attention [10,11]. But for practical applications, it is very important to develop Si_3N_4 with low dielectric constant (ε) and low dielectric loss (tan δ) since the dielectric absorption of microwave power leads to inhomogeneous temperature profiles and can damage the quality of the products [12].

Pore design is considered as an effective way to decrease dielectric constant. It is well known that the dielectric constant is mainly dependent on porosity in porous ceramics [13–15]. Furthermore, dielectric constant is also affected by pore morphology. Spherical pores exhibit higher piezoelectric coefficient and remnant polarization compared with irregular pores [16]. Polymethyl methacrylate (PMMA) is a kind of spherical particles and can be easily burned out. Compared with other preparation method of porous Si_3N_4 ceramics, e.g., carbothermal nitridation [17]; combustion synthesis [18]; *in situ* reaction bonding [19]; freeze casting [20], the porosity and the pore size can be easily controlled by adjusting the content and the size of adding PMMA. So it is a good way to prepare porous Si_3N_4 ceramics with low dielectric constant by adding PMMA as pore former.

In this paper, porous Si_3N_4 ceramics with controlled porosity were fabricated by liquid phase sintering. The phase composition, microstructure, mechanical and dielectric properties as a function of porosity were investigated. To keep the α:β-Si_3N_4 ratio and the content of liquid phase, samples sintered at 1800 °C with 5% additives were chosen to study the influence of porosity on flexural strength and dielectric constant.

2. Experimental procedure

α-Si_3N_4 (SN-E10, purity $> 99.5\%$, α ratio $> 95\%$, average particle size of 0.5 μm; UBE Industries, Ltd., Tokyo, Japan), Y_2O_3 (purity ≥ 99.99 wt%; Yuelong company, Shanghai, China, average particle size of 3 μm) and Al_2O_3 (purity $> 99.9\%$, α ratio $> 95\%$, average particle size of 0.5 μm; Wusong Fertilizer Factory, Shanghai, China) were used as the starting materials. Al_2O_3:Y_2O_3 in the fixed mole ratio of 2.98:1 were used as sintering additives with the content of 3, 5, 10 wt%. Polymethyl methacrylate (PMMA, Shanghai

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Coral Factory, Shanghai, China) with the particle size of 425–250 μm, 150–250 μm and 150–74 μm were used as pore formers. A mixture of α-Si_3N_4, Al_2O_3, Y_2O_3 and PMMA was ball-milled in ethanol for 24 h. After dried and sieved through a screen, the powder was pressed into rectangular bars with dimensions of 5.0 × 6.0 × 45.0 mm at100 MPa. The bars were firstly heated at 600 °C in air with a heating rate of 2 °C/min for 3 h to burn out the PMMA and then sintered at 1700–1850 °C in 0.5 MPa nitrogen atmosphere for 2 h at a heating and cooling rates of 5 °C/min. Samples were machined into a rectangle bar with dimension of 3.0 × 4.0 × 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 mm and a cross-head speed of 0.5 mm/min were used. The porosity and bulk density were determined by the Archimedes method using distilled water as medium. Phase analysis was conducted by X-ray diffraction (XRD) (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 dielectric constant and dielectric loss of the samples with the size of $\Phi 3.00 \times 30.00$ mm were measured in the frequency range of 1.96–12.1 GHz at room temperature by RF impedance/material analyzer (Model E8363A, Agilent, USA). The pore size distribution was determined by mercury porosimetry (Model pore sizer 9320, Micrometritics Co. Ltd., USA).

3. Results and discussion

Fig. 1 shows the XRD pattern of porous Si_3N_4 ceramics prepared at different sintering temperature. It can be seen that the phase transformation from α-Si_3N_4 to β-Si_3N_4 is completely accomplished. In addition, an obvious peak of $Y_2Si_3O_3N_4$ was found [21]. This can be explained that added Y_2O_3 reacts with the SiO_2–Si_3N_4 [22]. The SiO_2 is from the surface of Si_3N_4 particle.

Fig. 2 shows the microstructure of porous Si_3N_4 ceramics. It can be seen that the β-Si_3N_4 grains are fine with little additive; and it grows up with more additive. Solution-reprecipitation, which is controlled by the diffusion of Si and N ions through the boundary phase, is thought the main growth mechanism of β-Si_3N_4 in liquid phase [23]. So the content of liquid phase influences the morphology of β-Si_3N_4 grains.

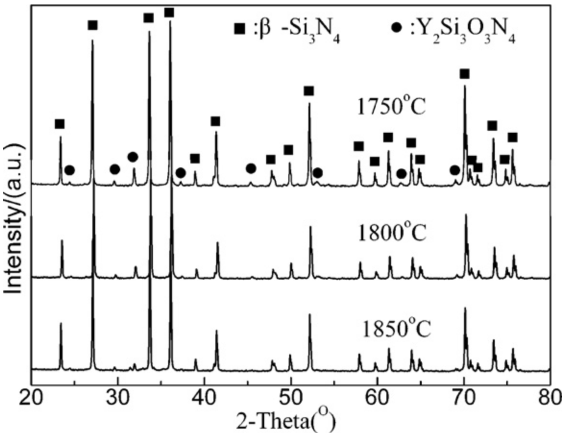

Fig. 1. XRD pattern of porous Si_3N_4 ceramics at different sintering temperature.

Fig. 3 shows the pores microstructure of decomposing PMMA. In the case of samples containing 300 μm PMMA, only a small quantity of pores is visible. And more spherical pores are observed in Fig. 3(b) because more small size PMMA is added. Some pore shape deforms because the thin wall of pore slumps owing to liquid-phase sintering in high temperature when large size PMMA is burned out. In sintering process, the pore is deformed owing to shrinkage. With pore size increasing, the deformation area of pore increase. And the deformation result in pore slumps. So the porosity and pore size can be controlled by adding pore formers.

Fig. 4 shows the flexural strength of porous Si_3N_4 ceramics. It is considered that porosity, pore size, intrinsic strength of the materials (grain and grain boundary) and microstructure are typical four determining factors for the strength of porous ceramics [24]. Regarding to the samples with different PMMA content, porosity and microstructure are the main influencing factors for the strength. It is well known that the strength decreases exponentially with increasing the porosity. Normally, more additives result in lower porosity. Furthermore, the microstructure also affects the strength. The fibrous β-Si_3N_4 grains, as whiskers, are helpful to the strength of ceramics. Typically, specimens with longer β-Si_3N_4 grains have higher strength with the same porosity [24].

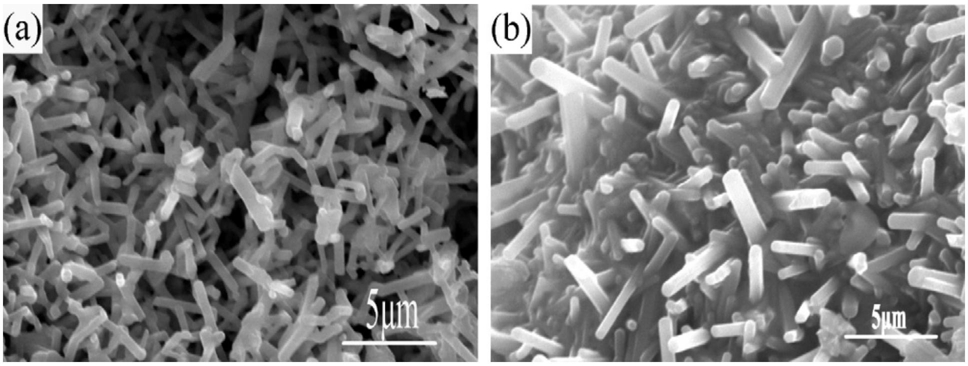

Fig. 2. The microstructure of porous Si_3N_4 ceramics: (a) 3 wt% (Y_2O_3 + Al_2O_3)–10% PMMA (74 μm) at 1800 °C; (b) 10 wt% (Y_2O_3 + Al_2O_3)–10% PMMA (74 μm) at 1800 °C.

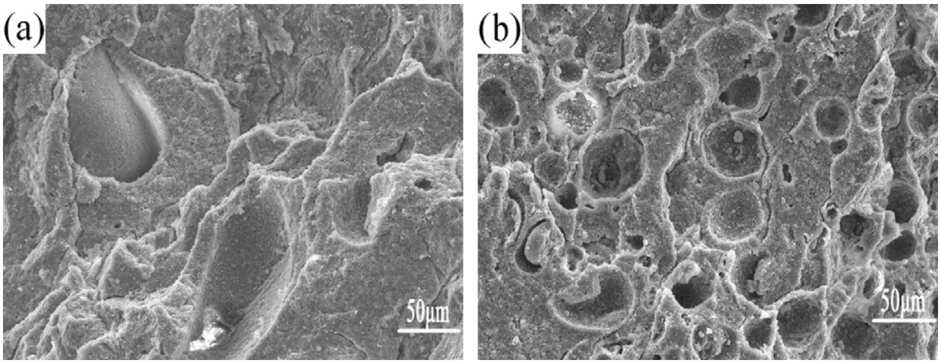

Fig. 3. The microstructure of porous Si_3N_4 ceramics: (a) 5% (Y_2O_3 + Al_2O_3)–30% PMMA (300 μm) at 1800 °C; (b) 5% (Y_2O_3 + Al_2O_3)–30% PMMA (74 μm) at 1800 °C.

As shown in Fig. 5, with increasing the content of PMMA, the porosity of ceramics increases and the flexural strength decreases. The relation between flexural strength (σ) and porosity (P) can be expressed as following equation [25,26]:

$$\sigma = \sigma_0 \exp(-\beta P) \tag{1}$$

where σ_0 is the flexural strength at a porosity of 0 and β is the structural factor. It can be seen from Fig. 6 that flexural strength and porosity of porous Si_3N_4 ceramics approximately fit the Eq. (1). But there are two data deviating from the line in Fig. 6. One is lower than normal value because the pore size is larger, and the other one is higher than normal value because the pore size is smaller. It can be seen from Fig. 3 that the size of residual pore is similar to the size of adding PMMA.

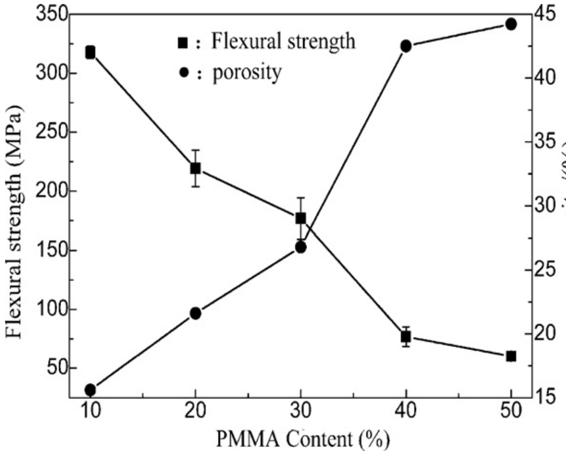

Fig. 5. The flexural strength and porosity of porous Si_3N_4 ceramics sintered with different content PMMA.

Fig. 7 shows the relationship between the dielectric constant (ε) of samples and the frequency. It can be seen that the dielectric constant is less dependent on the frequency. As the frequency increases, the dielectric constants almost keep the same. Samples with different dielectric constant are mainly due to the gradual introduction of air filled pores in the matrix, which increases the porosity and affects dielectric constant. If the pores are spherical and considered as a second phase, the dielectric constant can be expressed as following equation [27]:

$$\varepsilon' = \varepsilon_m \left[1 - \frac{3P(\varepsilon_m - 1)}{2\varepsilon_m + 1 - P + P\varepsilon_m} \right] \tag{2}$$

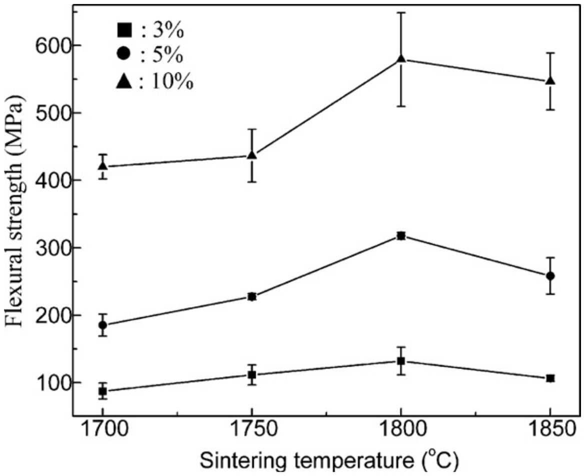

Fig. 4. The flexural strength of porous Si_3N_4 ceramics sintered at different temperature with different content additives.

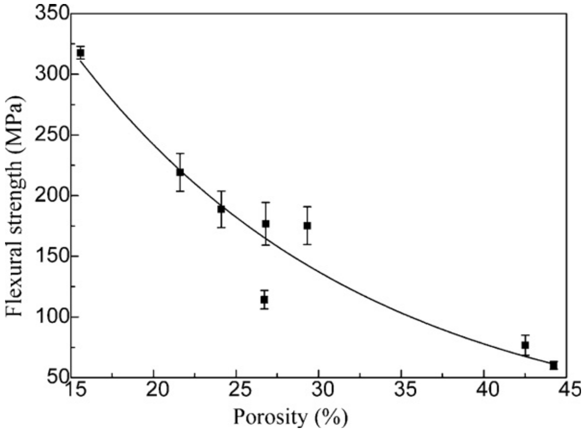

Fig. 6. The relationship between flexural strength and porosity with 5% (Y_2O_3 + Al_2O_3) at 1800 °C.

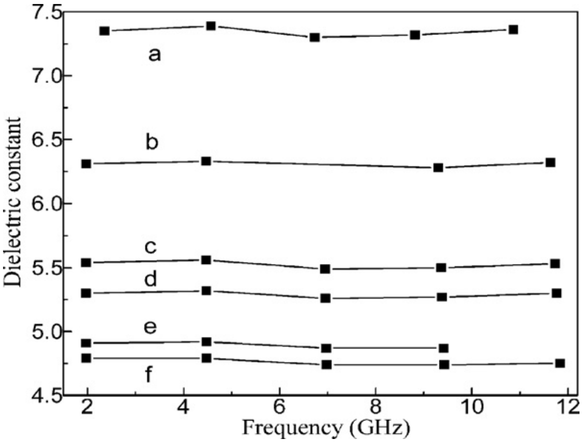

Fig. 7. The dielectric constant of porous Si_3N_4 ceramics: (a) 10% $(Y_2O_3 + Al_2O_3)$–10% PMMA at 1800 °C, (b) 5% $(Y_2O_3 + Al_2O_3)$–10% PMMA at 1800 °C, (c) 5% $(Y_2O_3 + Al_2O_3)$–30% PMMA (150 μm) at 1800 °C, (d) 5% $(Y_2O_3 + Al_2O_3)$–30% PMMA (300 μm) at 1800 °C, (e) 5% $(Y_2O_3 + Al_2O_3)$–30% PMMA (74 μm) at 1800 °C, (f) 3% $(Y_2O_3 + Al_2O_3)$–10% PMMA at 1800 °C.

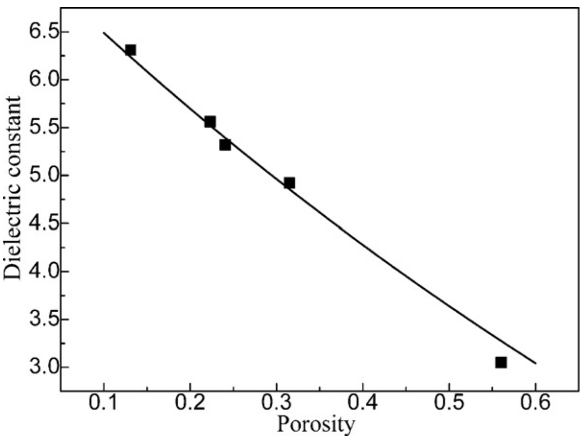

Fig. 8. The relationship between dielectric constant and porosity with 5% $(Y_2O_3 + Al_2O_3)$ at 1800 °C.

where ε' and ε_m is the dielectric constant of porous and fully dense materials, respectively, and P is the porosity. It can be seen from Fig. 8 that this is a good fit to the data. And it proved that the dielectric constant of porous Si_3N_4 ceramics decreases with porosity.

4. Conclusions

Porous Si_3N_4 ceramics with controlled porosity were prepared by adding PMMA as pore-forming agent. The porosity and pore size were successfully controlled by the sintering temperature, sintering additives and adding PMMA. The porous ceramics had high porosity with fine β-Si_3N_4 grains at low sintering additive. The flexural strength decreased exponentially with increasing the porosity and increased with smaller pore size. The dielectric constant is mainly dependent on the porosity, but less dependent on the frequency.

Acknowledgements

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