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# Effects of pore shape and porosity on the dielectric constant of porous β-SiAlON ceramics

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ABSTRACT

Gradient porous and homogeneous porous β-SiAlON ($Z=2$) ceramics were successfully fabricated through the unidirectional freezing of camphene-based suspensions at 0 °C and −196 °C, respectively. The dielectric constant of the porous β-SiAlON ceramics was investigated as a function of the pore shape and porosity. The dielectric constant decreased with increasing porosity, and the gradient porous β-SiAlON ceramics with channel and dendritic pores exhibited lower dielectric constants than homogeneous samples with irregular pores. The dielectric constants of the gradient porous β-SiAlON ceramics were found to be in good agreement with the prediction of the modified cubes model. The dielectric constant of the porous β-SiAlON ceramics was associated not only with porosity and pore shape, but also with pore anisotropy. The value of dielectric loss was not sensitive to porosity. These results have practical value for fabricating and optimizing porous ceramics on specific applications.



## 1. Introduction

Porous silicon nitride-based materials or SiAlON ceramics are recognized as a promising candidate for a wide range of applications that involve high temperature and corrosive environments, such as molten-metal filtrations, sensors, catalyst supports, separation membranes, light weight structural components and radome, due to their good thermal shock resistance, high strain tolerance, high strength and corrosion resistance [1–4].

Porous SiAlON ceramics are conventionally fabricated based on a straight forward processing route through the partial sintering of powder mixtures [5]. In this process, it is challenging to control the porosity and pore shape. However, for porous β-SiAlON ceramics, it is important to tailor the porosity and the pore structures to meet the specific application demands, such as good permeability, large surface area and low dielectric constant.

Over the last few years, the freeze casting process has attracted considerable focus in a wide variety of ceramic materials such as $Al_2O_3$, $Si_3N_4$, SiC, and $ZrO_2$ [6]. The popularity of this process has grown because the microstructures are easily tunable by varying the solvent and processing parameters, which results in complex pore structures and component geometries where the pores are a replica of the solvent crystals.

Due to the unique crystal growth characteristics of different solvents, the pore microstructure is lamellar when water is used as a solvent [7]; a dendritic structure is formed in the case of camphene [8]; and, long straight prisms are obtained when using TBA (*tert*-butyl alcohol) as a solvent [9]. Additionally, the pore microstructure can be tailored by properly controlling the freezing conditions to form either homogeneous or directional microstructures [10]. When the freezing conditions are controlled to achieve a minimum temperature gradient throughout the sample and the particles offset particle expulsion from the freezing front, the directional growth of solidified solvent is inhibited and homogenous microstructures with interconnected pores can be fabricated. When the anisotropic growth of a solidifying solvent is favored by the temperature gradient, a well-defined directional microstructure is also able to be fabricated.

To date, the nucleation and crystal growth of aqueous systems have been studied extensively. However, a clear understanding of the kinetics and mechanisms of the camphene growth process during freeze casting is lacking. Conversely, most papers concentrate on the mechanical properties of porous ceramics fabricated by freeze casting [11,12]. Nevertheless, there are relatively few results concerning about the effects of pore shape on the dielectric properties of porous $Si_3N_4$-based ceramics [3].

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In this article, porous β-SiAlON ceramics with homogenous and gradient pore structures were fabricated through the unidirectional freezing of camphene-based suspensions at different temperatures. The objectives of the present study were to demonstrate the difference in both porosity and pore morphology between porous β-SiAlON ceramics frozen at different temperatures, and to evaluate the dependence of the dielectric constant on the pore microstructure.

## 2. Experimental procedure

α-$Si_3N_4$ (5 wt% β, $d_{50}$ = 0.50 μm, Junyu Ceramic Co., Ltd., Shanghai, China), $Al_2O_3$ (grade A16SG, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and AlN (grade C, H. C. Starck, Berlin, Germany) were used as the starting materials to fabricate the porous β-SiAlON ($Si_{6-z}Al_zO_zN_{8-z}$, $Z = 2$) ceramics. Freeze casting of ceramic green bodies was performed using camphene ($C_{10}H_{16}$) without any further purification (95% purity, Guangzhou Huanpu Chemical Factory, Guangzhou, China) as the solvent, and HAOFAST923 (Shanghai Haoyang Co., Ltd., Shanghai, China) as the dispersant (1 wt% based on the total weight of the ceramic powders).

Different initial solid loading content slurries (10 vol%, 20 vol%, 30 vol% and 40 vol%) containing the β-SiAlON precursors were ball milled at 60 °C for 24 h in sealed bottles. The prepared slurries exhibited stable and excellent flowability for casting.

Unidirectional solidification was performed by pouring the resultant warm slurries into polyethylene molds (60 mm Ø × 20 mm) placed on a copper plate which maintained at 0 °C using an ice–water mixture or at −196 °C using liquid nitrogen. To eliminate the influence of the temperature gradient in the radial direction, the polyethylene molds were packed by a heat barrier layer on the surrounding side and were pre-warmed at 60 °C prior to placing them on the cold copper plate. Therefore, the slurry froze from the cold bottom with camphene crystals.

Thereafter, the green bodies were placed on a polyurethane sponge in open air at room temperature for approximately 4 days to eliminate the solidified camphene. Sintering was performed in a conventional graphite resistance furnace at 1800 °C for 2 h under a nitrogen gas pressure of 0.4 MPa. A BN–$Si_3N_4$ powder bed (50 wt% BN, 50 wt% $Si_3N_4$) was used. The heating and cooling rates were both 10 °C/min.

The densities of the sintered samples were calculated using mass and volume measurements. Pore size distribution was measured using mercury porosimetry (Autopore9500, Micromeritics Co., UAS). The crystalline phases of the sintered porous ceramics were characterized by X-ray diffraction (XRD). The microstructures of the sintered samples were observed using scanning electron micro scope (SEM). The pore size in different regions of the specimens was also determined by measuring the average size of the pores from the SEM micrographs.

The dielectric properties of the obtained porous β-SiAlON ceramics were measured using the wave guide method with a vector network analyzer (Agilent E8362B) over 12.4–18 GHz. The sizes of the measured samples were 7.9 mm × 15.8 mm × 2.0 mm. The measuring direction was parallel to the solidification direction of the samples. The test specimens were taken from the central zone of the sintered samples. Additionally, in order to reduce measurement errors to minimum, the measured samples are finely processed in our experiment to reduce the gap between sample and waveguide wall. In this study, on account of the big discrepancy among samples with different porosity and pore shape, the systemic errors are not strong enough to impact the analysis of influence of porosity and pore shape on dielectric constants.

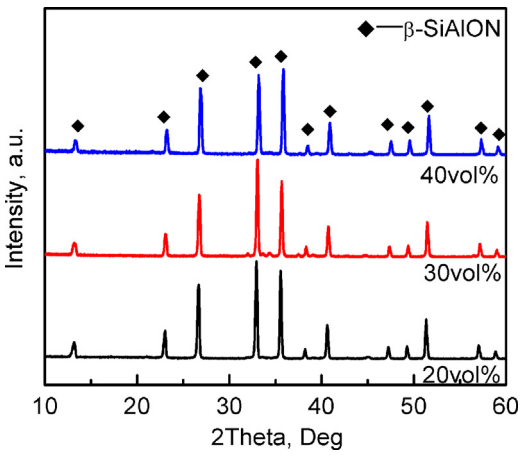


**Fig. 1.** XRD patterns of the sintered porous β-SiAlON ($Z = 2$) ceramics with different initial solid loadings frozen at −196 °C.

## 3. Results and discussion

### 3.1. Phase formation

Fig. 1 shows the XRD patterns of the sintered porous β-SiAlON ($Z = 2$) ceramics with different initial solid loading that were frozen at −196 °C (liquid $N_2$). Only β-SiAlON phase was detected in the samples with initial solid loadings of 20 vol%, 30 vol%, and 40 vol%, which indicates that the raw ceramic $Si_3N_4$, $Al_2O_3$, and AlN powders reacted completely to form the target phase, β-$Si_4Al_2O_2N_6$.

When the samples were prepared by freezing at 0 °C (ice–water mixture), all of the samples showed very similar patterns (Ref. [13] (Fig. 1)) [13], which means that all of the samples consisted of the β-SiAlON phase and no other secondary phases, regardless of the freeze temperature, predicating the freezing temperature did not influence the reaction of the raw ceramic powders and the formation of the β-SiAlON ($Z = 2$) phase.

### 3.2. Porosity and porous microstructure

The porosities of the sintered porous β-SiAlON ($Z = 2$) ceramics frozen at 0 °C or −196 °C with different initial solid loadings are listed in Tables 1 and 2. The porosity of the sintered porous β-SiAlON ceramic decreased proportionally with the increase in the initial solid loading. Compared with the samples frozen at −196 °C, the resultant porosity of samples frozen at 0 °C was lower given the same initial solid loading. Additionally, the porosities

**Table 1**
Porosity of porous β-SiAlON ($Z = 2$) ceramic frozen at −196 °C.

| The solid loading content (vol%) | Porosity[a] (%) | Porosity[b] (%) |
|---|---|---|
| 20 | 52.9 | 45.4 |
| 30 | 38.1 | 32.7 |
| 40 | 27.5 | 23.6 |

[a] measured by Archimedes' s method.
[b] measured by mercury intrusion porosimetry.

**Table 2**
Porosity of porous β-SiAlON ($Z = 2$) ceramic frozen at 0 °C.

| The solid loading content (vol%) | Porosity[a] (%) | Porosity[b] (%) |
|---|---|---|
| 10 | 71.3 | 63.5 |
| 20 | 47.0 | 44.8 |
| 30 | 36.1 | 32.1 |

[a] Measured by Archimedes' s method.
[b] Measured by mercury intrusion porosimetry.

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