



Progress in Preparation and Properties of Porous Silicon Nitride Ceramics

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Abstract

Porous silicon nitride ceramics is a promising functional ceramic material. In recent years, the research on the preparation of porous silicon nitride ceramics within different methods has been widely investigated. First, this work reviews the main synthesis methods of Si_3N_4 porous ceramics in detail, and compares the differences between strength and porosity caused by each method. The characteristics and advantages of different technologies under the current conditions were evaluated. Second, the dielectric properties, sound absorption properties and permeability properties of silicon nitride ceramics were compared and summarized based on the experimental results. Third, the applications fields of porous silicon nitride ceramics, such as smelting industry, catalyst carrier, sound absorption, wave-transparent, and biomedical fields were explored. Finally, the assessment of different silicon nitride ceramics preparation technologies was elaborated. This review gives an outlook on the porous silicon nitride ceramics, which shows great potential for further research in this field.

Keywords Porous silicon nitride ceramics · Porosity and strength · Reaction sintering method · Sound absorption · Dielectric property

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1 Introduction

Silicon nitride (Si_3N_4) ceramic are known as the "all-round champion" of ceramic materials, which exhibits excellent high temperature structural property. Si_3N_4 powder is the basic material for manufacturing silicon nitride ceramics [1, 2]. Si_3N_4 has three crystal structures, which are α - Si_3N_4 , β - Si_3N_4 and γ - Si_3N_4 phases. Their crystal configurations are shown in Fig. 1. The cell consists of a Si–N connected tetrahedron and in which the silicon atom at the center is surrounded by N atoms [3]. Three tetrahedral basic structural units share an N atom to form a solid structure [4].

When porous Si_3N_4 ceramic is sintered at high temperature, the granular α - Si_3N_4 undergoes a phase transition to the long columnar β - Si_3N_4 and forms the braided interlocking structure of porous silicon nitride ceramics [5]. This phase transition involves the fracture and formation of Si–N bonds. However, for silicon nitride materials, high-energy covalent bond is an unfavorable factor in the sintering process. The existence of Si–N covalent bonds leads to the lower atomic diffusion coefficient than that of other ceramics, which is also the most important reason for the difficulty of sintering silicon nitride ceramics [6, 7]. Therefore, the preparation

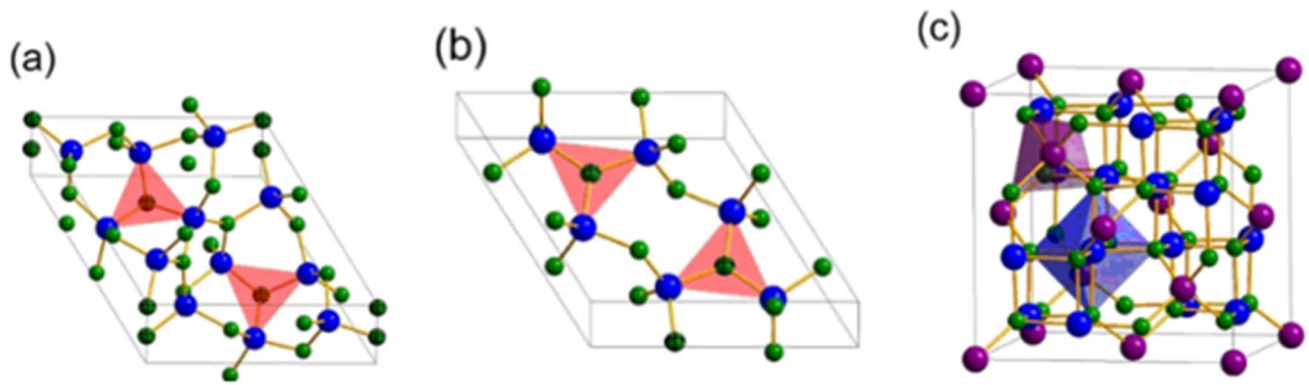


Fig. 1 **a** α - Si_3N_4 , **b** β - Si_3N_4 , **c** γ - Si_3N_4 the crystal structure, blue and purple spheres represent silicon atoms and green spheres represent nitrogen atoms [4]

methods of porous Si_3N_4 ceramics are different from that of other porous ceramics, such as porous oxide ceramics. Moreover, porous silicon nitride ceramics has the characteristic of light weight, strain tolerance, thermal shock resistance. In recent years, with the development of technology, the stability and reliability of the porous silicon nitride ceramics are improved, and its application fields are constantly explored and expanded. However, the latest research progress of porous silicon nitride ceramics is rarely reviewed at present.

This article reviews and compares the preparation methods, related properties and its application of porous silicon nitride ceramics. The review begins with a brief introduction and then various methods to the porous Si_3N_4 ceramics are introduced. Afterward, different forming methods in the preparation process of porous Si_3N_4 ceramics are stated and compared in detail. Subsequently, their novel and excellent properties are highlighted and wide applications of porous Si_3N_4 ceramics are summarized from the following aspects: smelting industry, filter material, radio-transmitting materials, catalyst carrier application, biomedical and sound absorption and noise reduction in extreme environments. Finally, the technological evaluation and outlooks of porous Si_3N_4 ceramic are proposed.

2 Preparation of Porous Silicon Nitride Ceramics

In the preparation process, the porosity, strength, pore size distribution and specific surface area of porous Si_3N_4 ceramics are the key index. Meanwhile, the morphologies of pores and other microstructures also play an important role on the properties [8]. Therefore, according to the different application fields, understanding the differences between preparation methods is beneficial to the preparation of high-performance porous silicon nitride ceramics. Based on the different formation processes of

pores, the main methods can be divided into two categories. One producing pores method is direct sintering and the other introducing pore method is by shaping, as shown in Fig. 2. According to the difference of initial materials, the former is mainly divided into phase change sintering method using α - Si_3N_4 as raw materials, the reaction sintering method using silicon powder as raw material and the carbothermal reduction method using silica and carbon as raw material. The latter is the introduction of pores by different ways before sintering, and then sintering at the high temperature. It can be divided into extrusion forming method, direct foaming method, freeze drying method, gel casting method, etc. In order to obtain porous silicon nitride ceramics with higher performance, the preparation process combining various methods is proposed. This part mainly introduces the two preparation methods.

2.1 Producing Pores via Sintering

2.1.1 Phase Change Sintering Method

Phase change sintering is a common method to prepare porous Si_3N_4 [8]. In this process, the granular α - Si_3N_4 of the green body changes into rod or fibrous β - Si_3N_4 under the action of sintering aids at the high temperature liquid phase. During the phase change, the pore structure and distribution are directly affected by the liquid phase migration of α - Si_3N_4 particles, the orientation growth and particle rearrangement of β - Si_3N_4 . Figure 3(a) shows the microtopography of porous Si_3N_4 ceramics prepared by phase change sintering. The elongated β - Si_3N_4 particles interweave with each other and form irregular through-hole structures in the way of bridging between the particles. Figure 3(b) is the corresponding XRD pattern. After sintering, α - Si_3N_4 was completely converted to β - Si_3N_4 in all samples regardless of

Fig. 2 Classification of preparation methods for porous silicon nitride ceramics

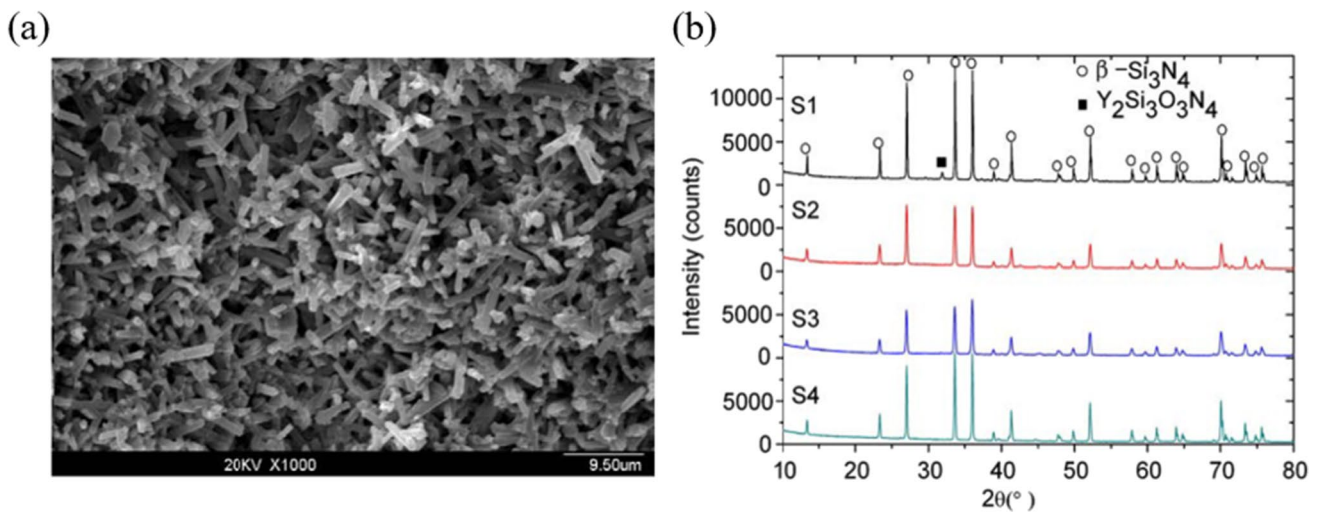
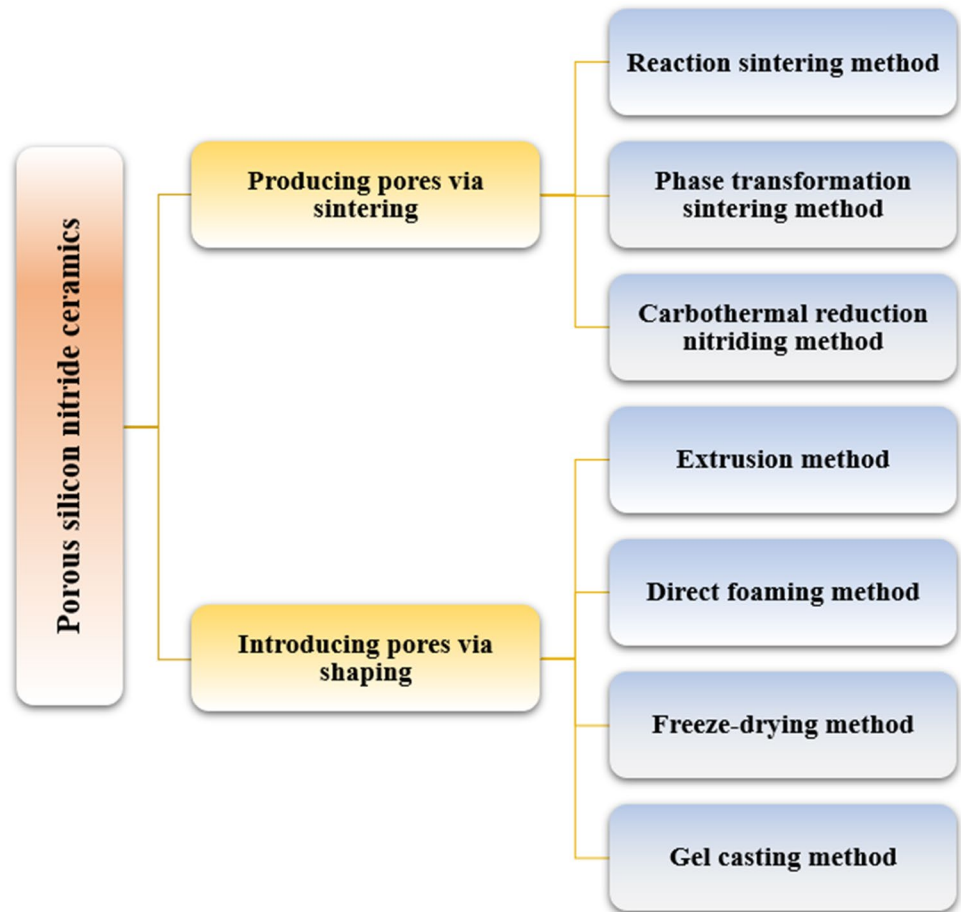


Fig. 3 **a** SEM of porous Si_3N_4 ceramics prepared by phase change sintering **b** the corresponding XRD pattern [9]

the formulation, no other phase was detected except a very small amount of $\text{Y}_2\text{Si}_3\text{O}_3\text{N}_4$ phase formed by the reaction between Si_3N_4 and Y_2O_3 in S1.

Quan et al. [10] investigated the effect of SiO_2 content formed in the oxidation process on the microstructure of Si_3N_4 . In this paper, using the $\alpha\text{-Si}_3\text{N}_4$ powder with average particle size of 0.7 μm and 1.0 μm and Lu_2O_3 as sintering

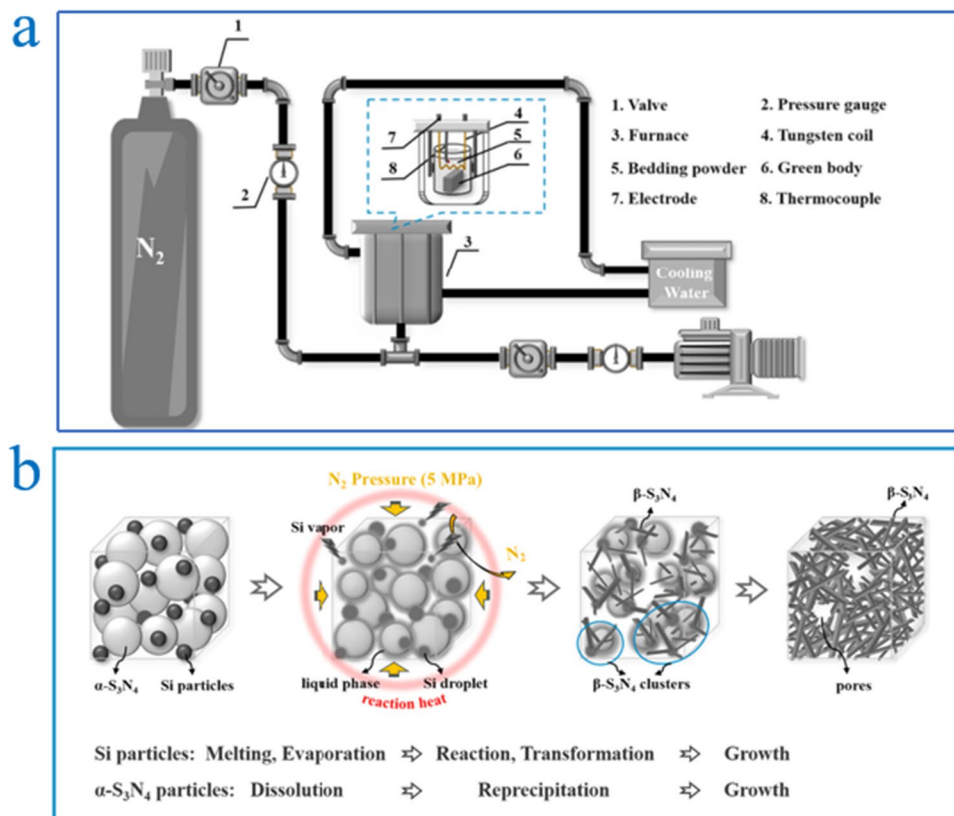
additive, and finally obtained a ceramics material with porosity of 40%–46% and bending strength of 92–207 MPa. A large amount of SiO_2 is favorable for the formation of secondary phase $\text{Si}_2\text{N}_2\text{O}$ and $\text{Lu}_2\text{Si}_2\text{O}_7$, and a small amount of SiO_2 is favorable for the formation of secondary phase $\text{Lu}_4\text{Si}_2\text{O}_7\text{N}_2$. The formation of secondary phase affects the microstructure and flexural strength of Si_3N_4 ceramics and the maximum flexural strength of porous Si_3N_4 materials containing secondary phase $\text{Lu}_4\text{Si}_2\text{O}_7\text{N}_2$ is 207 MPa. Yang et al. [11] investigated the effects of additive Yb_2O_3 content and temperature on mechanical properties of porous silicon nitride in sintering process. Porous Si_3N_4 ceramics have a porosity of 40–60% in the temperature range of 1600–1850°C. The results reveal that the ceramics prepared at 1700°C have the best properties, and the microstructure of the samples with high content of Yb_2O_3 show large and slender β - Si_3N_4 grains. However, the formation of $\text{Yb}_4\text{Si}_2\text{O}_7\text{N}_2$ crystal and the dissolution of Yb ions restrain the phase transition. When the content of Yb_2O_3 is 5 wt.%, the relative density of the prepared ceramics is 56.6%, and the corresponding bending strength is up to 371 MPa, and the average aperture is 0.3~0.5 μm . Wang et al. [12] prepared porous β - Si_3N_4 ceramics by combustion synthesis using Si powder, α - Si_3N_4 and Y_2O_3 powder as raw materials. The effects of α - Si_3N_4 diluent content on nitriding rate, shrinkage rate, porosity and bending strength of porous ceramics

were investigated. The results show that when the content of α - Si_3N_4 diluent is equal to that of Si, the porous β - Si_3N_4 ceramics have the 49% porosity and 151 MPa flexural strength by combustion synthesis. And the linear shrinkage of porous β - Si_3N_4 ceramics is only 2.8%. Due to the low shrinkage rate, large size and complex shape of near-net silicon nitride components can be produced at a low cost. Figure 4 are the schematic diagram of self-propagating combustion synthesis (SHS) device and the formation mechanistic diagram of pores Si_3N_4 by phase transition at the high temperature. Yang et al. [13] prepared porous silicon nitride (Si_3N_4) ceramics by atmospheric sintering method. By adjusting the content of solid phase and additives ($\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$), the porosity of porous Si_3N_4 sintered at 1650°C for 3 h is 39.28%, and bending strength is 146.0 MPa. The fracture toughness of this is 1.44 $\text{MPa m}^{1/2}$, and dielectric constant is 4.03 at 14 GHz.

2.1.2 Reaction Sintering Method

Another preparation method of porous Si_3N_4 is reaction sintering, and silicon powder was selected as the raw material to synthesize Si_3N_4 in nitrogen atmosphere [15]. The Si powder accumulates to form micron size pores. When sintering additives are added, the shapes of the pores are uneven and irregular. Figure 5 shows the typical micro-morphologies of

Fig. 4 a Equipment diagram of SHS device b Mechanism diagram of pore formation in device [14]



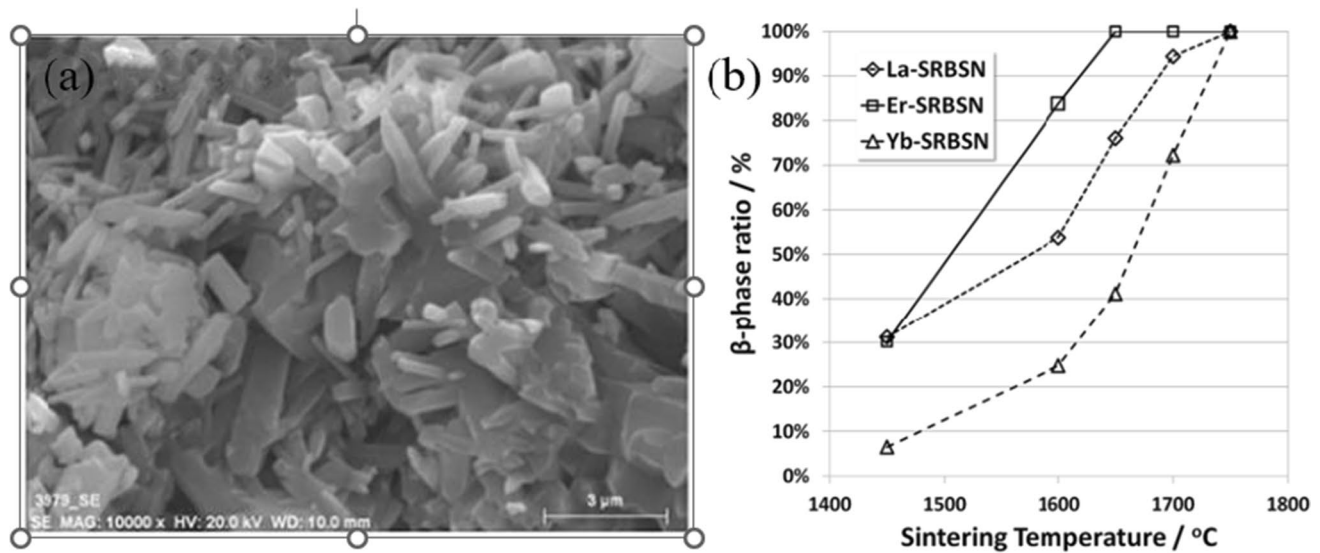


Fig. 5 a Typical micro-morphologies of porous Si₃N₄ ceramics prepared by reaction sintering b The α–β phase transformation behavior for different rare-earth oxides. (SRBSN: sintered reaction-bonded silicon nitride)

porous Si₃N₄ ceramics prepared by reaction sintering. The microstructure consisted of almost columnar β-Si₃N₄ grains, and columnar grains with high aspect ratio, which made up the entire structure.

Yao et al. [16] prepared near-net forming porous silicon nitride ceramics with complex shapes by the reaction sintering method. In order to inhibit the hydrolysis of Si, the butyl stearate (BS) coating method was introduced. The dispersion of Si was enhanced by ammonium polyacrylate (NH₄PAA) coating method. The results show that the Si hydrolysis is strongly inhibited by the 4 wt.% BS coating when the oxygen content decreases from 2.96 wt.% to 1.24 wt.%. The density of porous Si₃N₄ ceramics is 1.57–1.92 g/cm³ (the porosity is 50.9–40%), and the bending strength is 47–108 MPa. Meanwhile, the bending strength decreases with the decrease of the density. Lee et al. [17] systematically investigated the effect of silicon particle size on the β-Si₃N₄ ratio, microstructure and flexural strength of porous silicon nitride ceramics prepared by reaction sintering reintering (SRBSN). The particle size of the raw silicon powder is controlled by planetary milling, and then nitriding reaction is performed at different sintering temperatures. The results show that the apparent porosity of ceramics is proportional to the total volume of additives, while the β-Si₃N₄ ratio is independent of the total volume of additives. The bending strength is closely related to the evolution of long β-Si₃N₄ grains and the content of Yb element. The other key parameter is the molar ratio of SiO₂ to total oxide. When the molar ratio of SiO₂ to total oxide is less than 0.7, the rod-shaped β-Si₃N₄ particles are mainly grown and the flexural strength of 400 MPa can be obtained. The results and

analysis indicate that the initial silicon size is too small for the preparation of porous silicon nitride ceramics.

Zhang et al. [18] investigated the effects of nitrogen pressure and initial silicon particle size on the properties of porous silicon nitriding ceramics by combustion synthesis method. It was found that with the increase of N₂ pressure and the reaction temperature, the reaction speed increases, and the evaporation of molten Si accelerates. With the increase of grain average aspect ratio, the bending strength increases from 67 to 134 MPa. With the decrease of Si particle size, porous Si₃N₄ ceramics with flexural strength between 213 and 102 MPa and porosity between 42 and 48% were prepared. This method is cost-effective and time-saving.

With the initial Si particle size, the reaction mechanism varies. Figure 6 is a schematic diagram of the mechanism of silicon with different particle sizes to form porous Si₃N₄. Moreover, the content of sintering additives, the reaction temperature and gas atmosphere could all affect the pore structure and size formed of rod β-Si₃N₄. Figure 7 shows that the formation mechanism of silicon nitride by the reaction sintering method at the different temperatures. When the temperature is under the melting point of silicon, the silicon slowly volatilizes into Si vapor. Then it reacts with nitrogen and deposits on the surface of the whisker. Reaction sintering method has the characteristic of low-cost, near-size sintering to produce ceramic materials.

2.1.3 Carbothermal Reduction Method

The carbothermal reduction method applied SiO₂ and C powder as the main raw material [20]. At first, silicon was

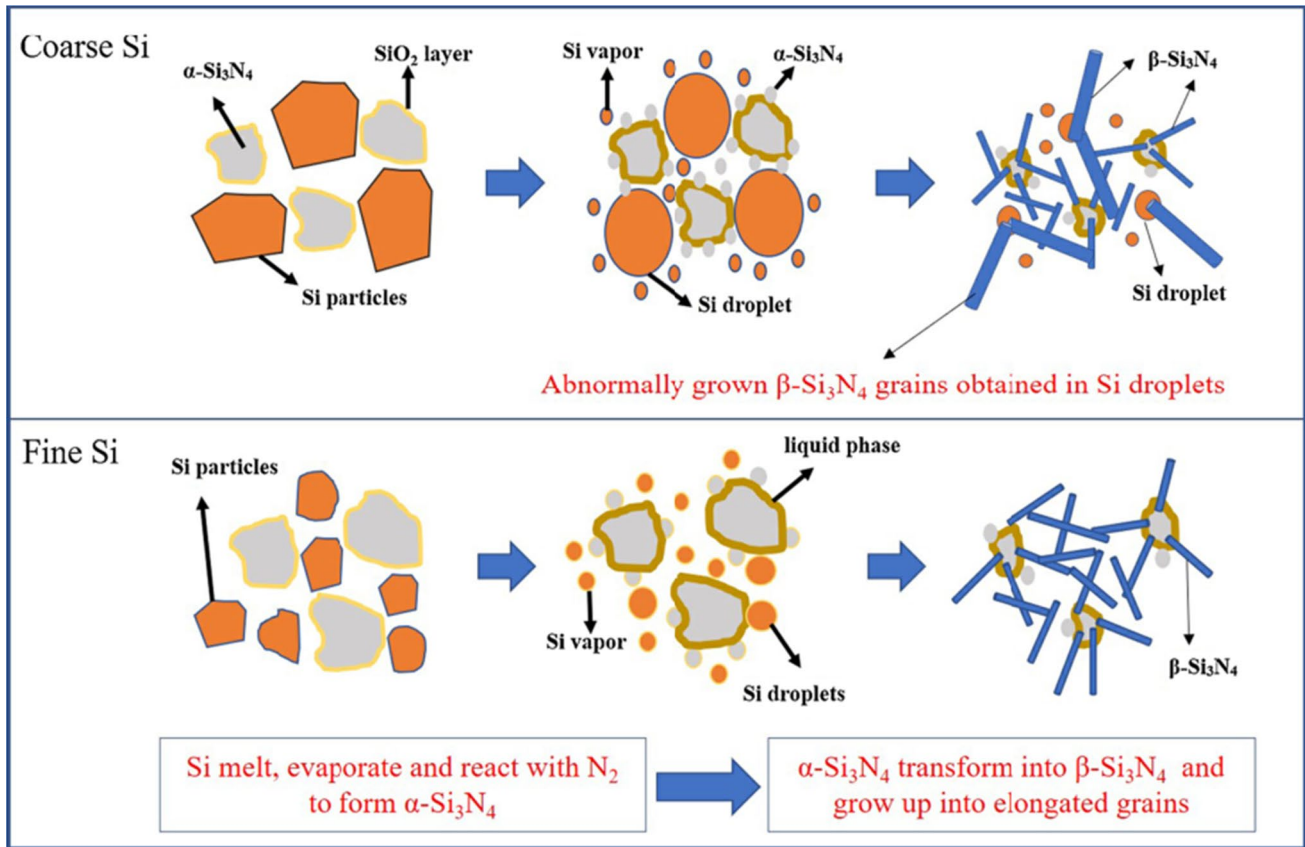


Fig. 6 Schematic diagram of the mechanism of porous Si_3N_4 formation starting with different Si particle sizes [18]

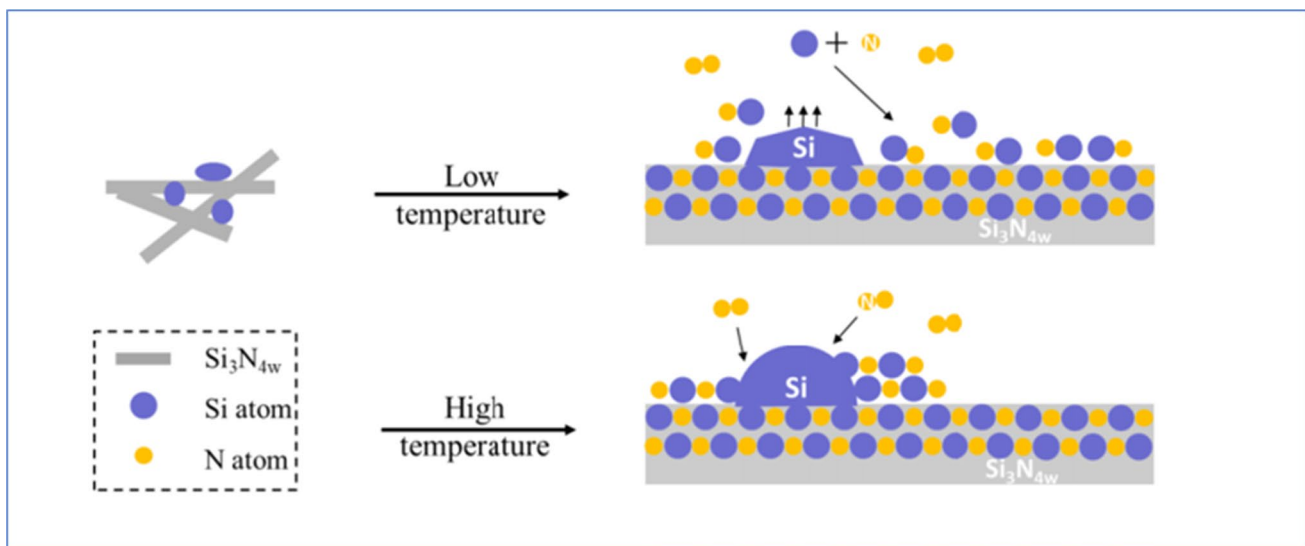
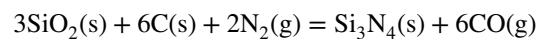


Fig. 7 Schematic diagram of the mechanism by which silicon at different temperatures begins to form porous Si_3N_4 [19]

produced from the carbothermal reduction process, then the porous silicon nitride ceramics were prepared under N_2 or NH_3 atmosphere [21]. The main reaction equation is as follows:



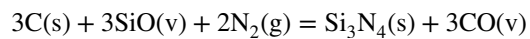
The silicon nitride produced by carbothermic reduction reaction acts as a diluent and can reduce the formation of

free silicon. This is beneficial to achieve the net size to produce the desired shape components. Figure 8(a) was the typical micromorphology of porous Si_3N_4 ceramics prepared by carbothermic reduction method. The sample occupied the coarse, conglomerated equiaxial $\beta\text{-Si}_3\text{N}_4$ grains. The pores were generated on the boundary of small rod-shaped $\beta\text{-Si}_3\text{N}_4$ particles, and the pore structure is irregular. In addition, a lot of $\beta\text{-Si}_3\text{N}_4$ phases and the minor of $\alpha\text{-Si}_3\text{N}_4$ phase were detected in Fig. 8(b). The grain boundary phase was identified as a crystalline $\text{Y}_8\text{Si}_4\text{N}_4\text{O}_{14}$, which was apparently formed by the reaction between Y_2O_3 , SiO_2 and Si_3N_4 .

Liu et al. [23] selected rice husk as raw materials, and prepared porous silicon nitride ceramics at 1500 °C. The results illustrate that the key factors are CeO_2 concentration and sintering temperature, and MgO-CeO_2 is a more effective sintering additive than MgO alone. Both α phase and β phase are generated at 1500 °C when CeO_2 concentration is 3%-5%, and α phase \rightarrow β phase transformation is completed at 1550°C. The optimum concentration of CeO_2 is 5% and the optimum sintering temperature is 1550°C. Under the optimum conditions, the strength and porosity of the porous ceramics are 84.09 MPa and 42.81%. Lu et al. [24] used low-cost diatomaceous earth and carbon black as raw materials to produce the porous silicon nitride ceramics with high porosity and uniform pore structure through carbothermal reduction reaction. It is obvious that with the increase of sintering additives Y_2O_3 content, the length-diameter ratio of $\beta\text{-Si}_3\text{N}_4$ columnar grains gradually decreased. In terms of mechanical properties, the shrinkage rate and bending strength gradually increase. Shan et al. [22] prepared porous silicon nitride ceramics with fibrous

interlocking structure by silicon dioxide carbothermic nitriding method. The effect of different starting powders on the microstructure and mechanical properties was investigated. The results show that the microstructure and mechanical properties of porous silicon nitride ceramics mainly depend on the size of raw materials. The mixture of SiO_2 and Carbon with large particle sizes resulted in obvious weight loss and shrinkage, which decreased the porosity and formed the $\beta\text{-Si}_3\text{N}_4$ microstructure with low aspect ratio and grain reunion. The porous silicon nitride ceramics prepared with fine initial powder have better interlocking microstructure and higher porosity. Porous Si_3N_4 ceramics prepared from fine Si_3N_4 powders have high porosity (71%) and flexural strength (24 MPa), which is mainly due to the formation of fine Si_3N_4 grains. Zhi et al. [25] prepared high pore ultrafine Si_3N_4 ceramics through the reaction of carbon nanotubes (CNTs) and SiO steam in nitrogen atmosphere. Figure 9 shows the schematic diagram of the reaction device and SEM image of the samples.

As can be seen from Fig. 9(a), silicon oxide powder was placed at the bottom of a graphite crucible and heated to produce SiO vapor. The CNTs preform is supported by thin graphite plates with holes and placed above the SiO powder, and then sintered at high temperature. The reaction equation is as follows:



Compared with the other carbothermic reduction reactions, most of the CNTs had been transformed into Si_3N_4 , the rod-like Si_3N_4 obtained has higher aspect ratio, and the

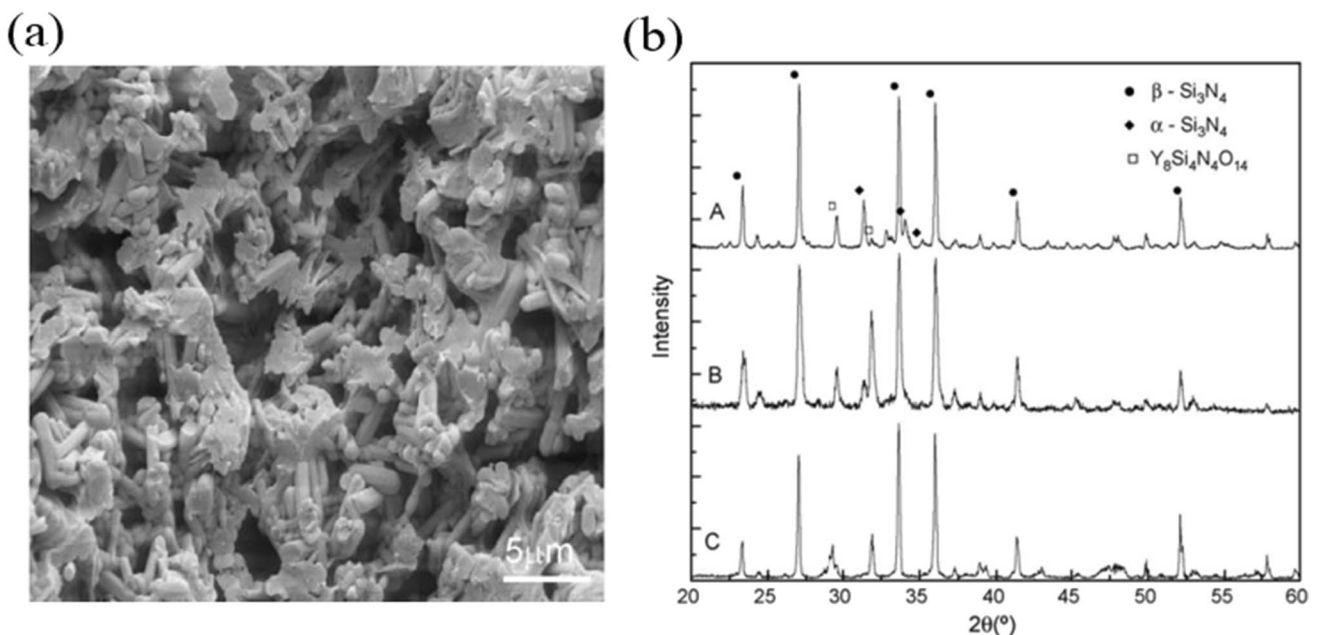


Fig. 8 Typical micromorphology of porous Si_3N_4 ceramics prepared by carbothermic reduction [22]

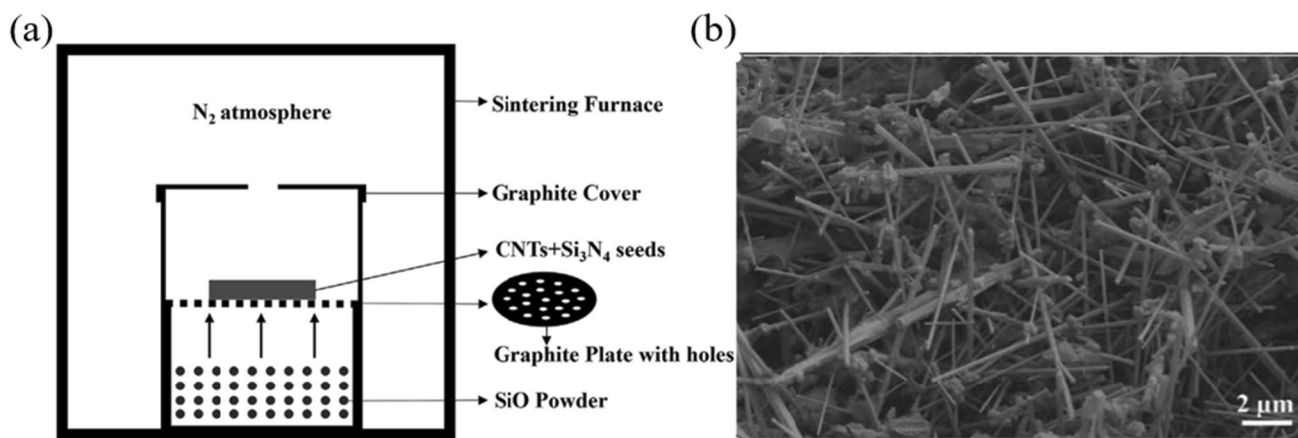


Fig. 9 **a** Schematic diagram of gas–solid reaction process under high pressure, **b** SEM topography of ultra-fine porous silicon nitride obtained [25]

rod-like and fibrous particles overlap each other to form a complete (3D) network with high porosity.

In general, the formula between strength and porosity is as follow:

$$\sigma = \sigma_0 \exp(-\beta p)$$

Where σ is the strength of the porous ceramic; σ_0 is the strength of the ceramic with a porosity of 0; β is the structure coefficient; and p is the porosity. Obviously, the strength decreases exponentially with the porosity increasing.

Figure 10 shows the corresponding relationship between porosity and strength of Si_3N_4 ceramics sintering method with different processes. As can be seen from the blue part of Fig. 10, the porosity of phase change sintering method with $\alpha\text{-Si}_3\text{N}_4$ as the starting material is maintained between 35 and 60%, and the strength is above 100 MPa. This is due to the interleaving structure formation of rod-shaped $\beta\text{-Si}_3\text{N}_4$, and the high $\alpha\text{-Si}_3\text{N}_4$ content is more favorable for the formation of $\beta\text{-Si}_3\text{N}_4$ with large diameter. The properties of porous Si_3N_4 prepared by phase change sintering method are depended on the additives, sintering temperature and forming process. This process is relatively simple and controllable to obtain the ceramics with higher strength. However, due to the high cost of raw $\alpha\text{-Si}_3\text{N}_4$ powder, the scale of the process is faced with great challenges.

The orange part of the Fig. 10 is the porous Si_3N_4 ceramics prepared using Si powder as raw material by different technologies. With silicon powder as raw material, the porosity of the reaction sintering method is between 30 and 60%, and the strength is under 250 MPa. The strength of the material was improved by secondary sintering method, which is reaction re-sintering method (SRBSN). As indicated by reference 18 in the figure, the ceramic strength after SRBSN can even reach 460 MPa. This is because

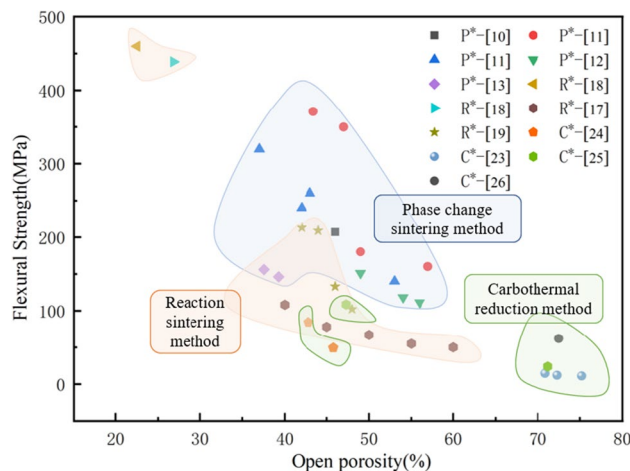


Fig. 10 Porosity and flexural strength of porous Si_3N_4 ceramics prepared of different technologies (P*:Phase change sintering method; R*:Reaction sintering method; C*:Carbothermal reduction method)

silicon powder to be nitrided into $\alpha\text{-Si}_3\text{N}_4$ and then to be sintered into $\beta\text{-Si}_3\text{N}_4$ by phase transformation sintering reaction. With the same porosity, the ceramic strength obtained by reaction sintering is slightly lower than that of phase change sintering. In this process, gas–solid reaction is combined, and the product is more complex. Under different preparation processes, Si_3N_4 particles and short rod $\beta\text{-Si}_3\text{N}_4$, fibrous $\alpha\text{-Si}_3\text{N}_4$ and $\text{Si}_2\text{N}_2\text{O}$ may be generated, and these reaction products are mixed to form porous structure.

As can be seen from the green part of Fig. 10, compared with the other two methods, the porosity of porous Si_3N_4 ceramics prepared by carbothermic reduction combined with different processes has higher porosity, but its strength decreases significantly. Its strength is mostly lower than 100 MPa, and its porosity can reach more than 70%. This is

because when using carbothermal reduction nitriding, the pores are formed not only by the accumulation of raw material powder and the intermixing of granular and rod-like products, but also relate to the large weight loss of reducing agent carbon. Therefore, the ratio of carbon to silicon dioxide in the raw material for powder production has active effect on the microstructure and mechanical properties of porous Si_3N_4 ceramics. In general, carbothermal reduction method has the characteristic of low cost, high operation safety to produce porous silicon nitride ceramics with excellent performance [26]. Also, the raw materials of carbothermal reduction method are non-toxic and harmless.

Table 1 summarizes the advantages and disadvantages of porous silicon nitride ceramics prepared with three different starting materials.

2.2 Introducing Pores via Shaping

The method of porosity introduction by shaping means that the pores are first artificially introduced into the ceramic embryo, and then the porous ceramics are finally formed by sintering. According to the different ways of introducing pores, it is mainly divided into the extrusion forming method [9], direct foaming method [29], freeze-drying method

[30–33], and gel casting method [13, 19, 34]. A comparison of the different forming methods is shown in Table 2.

Figure 11(a) shows the schematic diagram of the extrusion molding method. The extrusion molding method generally uses Si or Si_3N_4 as raw materials to make a paste at first. After that, the extruder was applied to conduct multi-channel extrusion forming process, which was generated directly from the macroscopic continuous channel in the body. At last, the ceramic with pores is formed by reaction sintering or phase change sintering process. Figure 11(b) shows the product diagram of the extrusion forming method. The Extrusion molding technology is mainly through the design of die to achieve the pore structure control of the product. Extrusion method is commonly used to produce ceramic products with constant cross-sectional area. Due to its high throughput and ability to manufacture complex products, it can replace current molding methods in some areas. For example, extrusion is widely used to manufacture cordierite catalytic converters, which can effectively control automobile exhaust emissions.

Figure 12 shows the flow chart and morphology diagram of foaming method. This can be seen in combination with Fig. 12(a), foam method is a way to introduce bubbles into a slurry of ceramic or precursor, and form a foam slurry. The shape of the foam slurry changes with the foaming agent. Some macromolecules, such as protein [40, 41] and starch

Table 1 Comparison of properties of three sintering processes

The sintering method	The main raw material	Porosity /%	Strength /MPa	Advantages	Disadvantages
Phase change sintering method [9–14]	$\alpha\text{-Si}_3\text{N}_4$	35–60	100–400 MPa	Uniform porosity High compressive and tensile strength; High creep resistance	High cost; Low permeability
Reaction sintering d [16–18, 18, 28]	Si powder	40–60	50–300 MPa	Low energy consumption; Low cost; High tensile strength	Complex pore structure; Low permeability
Carbon thermal reduction d [20, 22–24]	C + SiO_2	45–75	less than 100 MPa	Easy access to starting raw materials; Clean environmental protection; High porosity	Complex pore structure; Lower strength

Table 2 Comparison of different forming methods

Methods	Porosity /%	strength /MPa	Advantages and Applications
Extrusion molding [9]	30–50	60–150	Producing ceramic products with the constant cross-sectional area, high throughput and the ability to manufacture porous ceramics with honeycomb pore structure, widely used in the automobile exhaust filter
Direct foaming [29, 35]	70–90	10–30	With high permeability and specific surface area, it can be used as catalyst carriers, filters, and biological materials
Freeze drying [30–33]	60–90	6–65	The controllable dielectric constant and pore structure make it an ideal choice for high-speed aircraft electromagnetic wave transmission materials
Gel casting method [13, 19, 34, 36]	40–60	100–250	near clean shape and low-temperature molding, low processing cost, high bending strength, low dielectric coefficient, suitable for radome materials

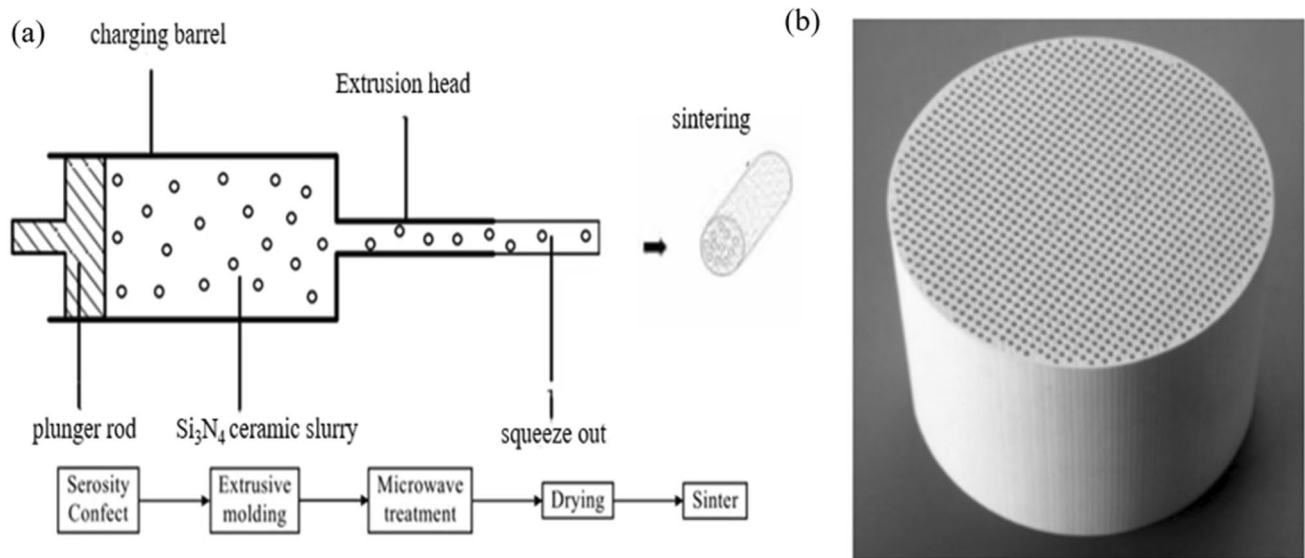


Fig. 11 **a** Schematic diagram of extrusion molding method [37, 38]; **b** the product diagram of extrusion forming method [39]

[42], can be used as foaming agents. The foam slurry is cured, dried and finally sintered to form porous Si_3N_4 ceramics. Figure 12(b) is the SEM of porous ceramics prepared by foaming method. The advantage of foaming method is that the porosity, pore size distribution and pore structure of its products can be adjusted in a large range.

Freeze-drying method is a wet-forming process to get complex shapes in recent years. Figure 13(a) is a flow chart of a typical freeze-drying process. First of all, the $\alpha\text{-Si}_3\text{N}_4$, dispersants and binders are mixed, then the slurry is poured into a mold containing a metal cylinder with high thermal conductivity, which is immersed in liquid nitrogen. It is then freeze-dried under vacuum, where the ice is sublimed and the raw body is dewaxed, eventually sintered under high-temperature nitrogen pressure. It is formed by controlling the directional freezing of water or organic solvent in a certain direction to form neatly arranged solution crystals, and then the template is dried under low pressure. Finally, porous ceramics are obtained by high-temperature sintering process [43, 44]. Figure 13(b) is the SEM image of porous ceramics prepared by a freeze-drying method. In the figure, the porous structure of the lyophilized layered structure gradually transforms into a honeycomb structure. This changes the morphology of the material at the microscopic scale. It originates from the addition of glycerol changes the crystallization and solidification behavior of the slurry making ice grow in a honeycomb structure. After ice sublimation, a new type of honeycomb pores emerges, and the microstructure of the final material will change [33].

Gel casting is another way to add polymer organic monomer and crosslinking agent to Si_3N_4 ceramic powder slurry, which is mechanically mixed by ball milling and stirring

with an initiator and catalyst. After the ceramic slurry is injected into a complex mold cavity, the initiator reacts with organic monomer to generate a 3D network structure. When the slurry solidifies, the blank body with higher bending strength is formed. Then, the organic matter was removed through demoulding process. Finally, ceramic products are obtained by sintering [45]. Gel casting molding is considered to be one of the effective methods for preparing high-performance porous silicon nitride ceramics. Figure 14(b) shows the pore morphology of porous Si_3N_4 billet with a single directional arrangement of holes prepared by gel casting mold.

In addition to the above four methods, in order to prepare ceramics with more excellent properties, domestic and foreign scholars have conducted further research on the forming process, mainly including cold isostatic pressing [47, 48], reactive bonding [49], the addition of pore-forming agent [50], etc. For example, Han et al. [51] used foam-gel casting molding nitride method to prepare nano-whisker-based 3D porous silicon nitride ceramics with high porosity. Due to low cost, it can be used in the industrial production of new catalyst support, filter and heat insulation materials. Han et al. [52] combined gel casting molding and microwave nitriding for the first time and prepared porous Si_3N_4 ceramics with higher mechanical strength at 1273–1373 K. In addition, its relatively low thermal conductivity makes it a candidate for thermal insulation material. Zhou et al. [53] investigated the method of adding PMMA microspheres with different particle sizes as pore-forming agents combined with cold isostatic pressing. Finally, micrometer size homogeneous spherical porous Si_3N_4 with an average bending strength of 122 MPa and dielectric constant of 3 was obtained. This preparation process combines

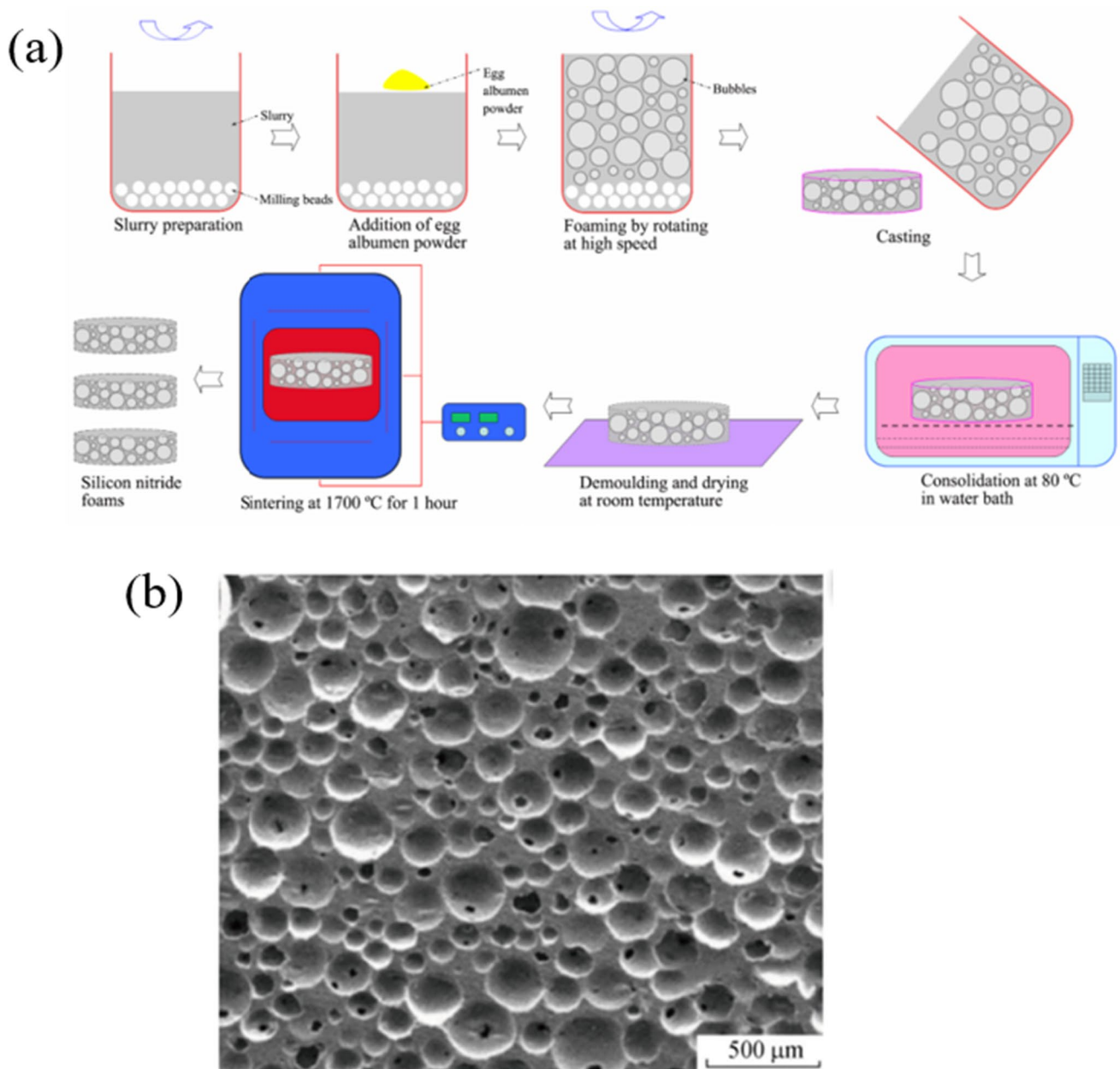


Fig. 12. **a** Schematic diagram of foaming method **b** the SEM of porous ceramics prepared by foaming method [35]

the advantages of a pore-forming agent, spray drying, and CIP (cold isostatic pressing), which shows great prospects for the preparation of porous Si_3N_4 ceramics with excellent properties in the industry.

3 Properties of Porous Silicon Nitride Ceramics

Porous silicon nitride ceramics have the characteristic of lightweight, strain tolerance, thermal shock resistance and other unique properties. It is a promising high-performance

material, and is widely used in the field of high-temperature wave transmission, molten metal filters, and catalyst carriers. Moreover, porous ceramics also have good sound absorption performance. The dielectric properties, sound absorption properties, and permeability properties were emphasized in this part.

3.1 Dielectric Properties

Dielectric properties are one of the most important indicators to evaluate the properties of wave-permeable materials. Moreover, the dielectric constant ϵ and loss tangent

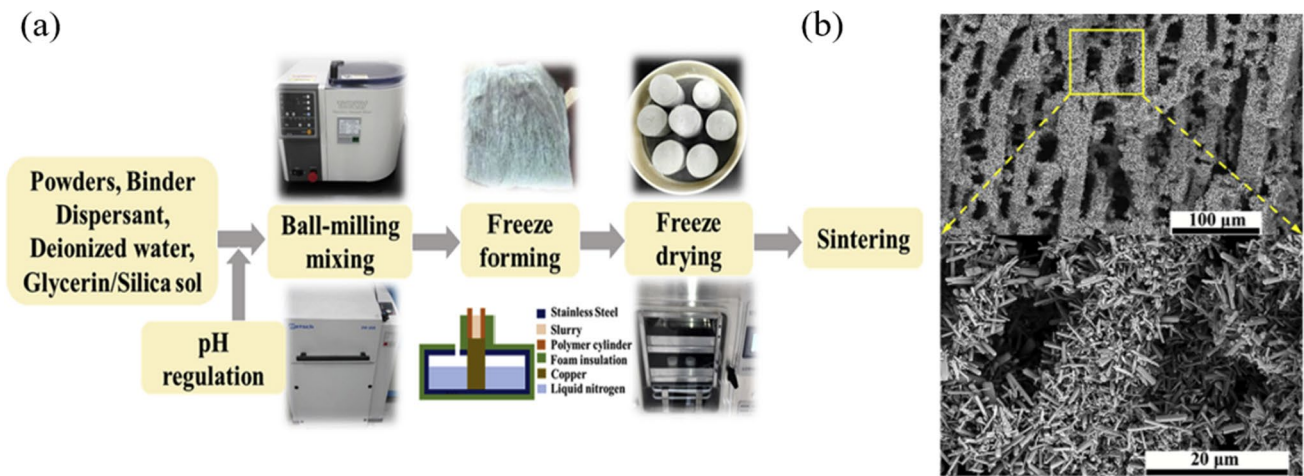


Fig. 13 a the flow chart of a typical freeze-drying process [32] b the SEM image of porous ceramics prepared by freeze-drying method [32]

$\tan\delta$ are the two most important parameters to evaluate the dielectric properties of a material [34]. Dense sintered Si_3N_4 ceramics exhibit excellent mechanical properties (bending strength = 600–1000 MPa) and thermal stability (> 1300 °C). However, compared with other radome materials, such as SiO_2 ($\epsilon = 3.9\text{--}4.0$) and BN ($\epsilon = 3.1\text{--}4.5$), the dielectric constant of compact Si_3N_4 ($\epsilon = 7.96\text{--}8.59$) is relatively high, which will limit its application in the production of thick structural parts with thicknesses exceeding 5 mm. Because its total dielectric constant should be less than 6 [54]. Due to the introduction of pores, the dielectric constant of the porous silicon nitride ceramics was greatly reduced. Gel casting molding method is an attractive molding method to obtain a lower dielectric constant. Because it is a near-net shape process with high output and low processing cost. Zhang et al. [19] prepared porous silicon nitride ceramics with electromagnetic wave penetration by gel casting mode combined with in-situ nitriding reaction, whose bending strength and dielectric constant were 44.9 MPa and 2.7, respectively. Yin et al. [36] introduced $\beta\text{-Si}_3\text{N}_4$ seeds into ceramic matrix, and obtain porous Si_3N_4 ceramics with excellent mechanical and dielectric properties by gel casting molding. The flexural strength and fracture toughness respectively reach the highest values of 378.50 MPa and 8.54 MPa $\text{m}^{1/2}$, respectively. In the 8.2–12.4 GHz range, the dielectric constant and loss tangent of the ceramic with 6 wt.% slender seeds addition varied from 4.70–4.82 and 0.041–0.047, respectively. It shows good microwave penetration performance. Table 3 summarizes the dielectric properties of different preparation processes of porous silicon nitride. The gel casting process is the most common method to prepare excellent dielectric properties at present.

As shown in Fig. 15(a), it can be concluded that the dielectric constant and dielectric loss of sintered samples

decrease with the increase of porosity. In addition, Xiao et al. [28] found that the dielectric constant was related to the ratio of diameter to thickness of the hole. In Fig. 15(b), the diameter-thickness ratio (D/H) is defined as the ratio of the sum of two adjacent apertures to the wall thickness of the ceramic parts. As can be seen from Fig. 15(b), the dielectric loss of the material is negatively correlated with the ratio of diameter to thickness of the material. As the ratio of diameter to thickness increases, the space occupied by the pore increases. The reason for dielectric loss can be attributed to ionization loss and polarization loss. Among them, the main source of ionization loss is gas and the probability of gas dissociation and loss in the pore is relatively high. This is why high porosity and D/H ratio lead to better dielectric properties. Yang et al. [48] prepared Si_3N_4 porous ceramics using polymethyl methacrylate (PMMA) as pore forming agent by combining cold isostatic pressing and pressureless sintering in a nitrogen atmosphere. With the increase of PMMA content, porosity and dielectric properties improved and the micropores formed by the $\beta\text{-Si}_3\text{N}_4$ bridge and the large pores formed by a pore-forming agent are the main factors, which decreased the flexural strength and improved the dielectric properties of the materials.

The dielectric constant and flexural strength of porous Si_3N_4 ceramics in different studies are shown in Fig. 16 [13, 19, 28, 34, 39, 48, 56–66]. The number in Fig. 16 indicates the serial number of the specific reference. For example, the number 13 in the figure indicates that the strength of the ceramic material prepared in reference 13 is 136 MPa and its dielectric constant is 4.6. As shown in the figure, by improving the preparation process, the dielectric properties of the obtained ceramics can reach 4 or even lower in most works of literature, but the corresponding strength will be reduced, some of them have strengths of less than 100 MPa. The increase of flexural strength is always accompanied by

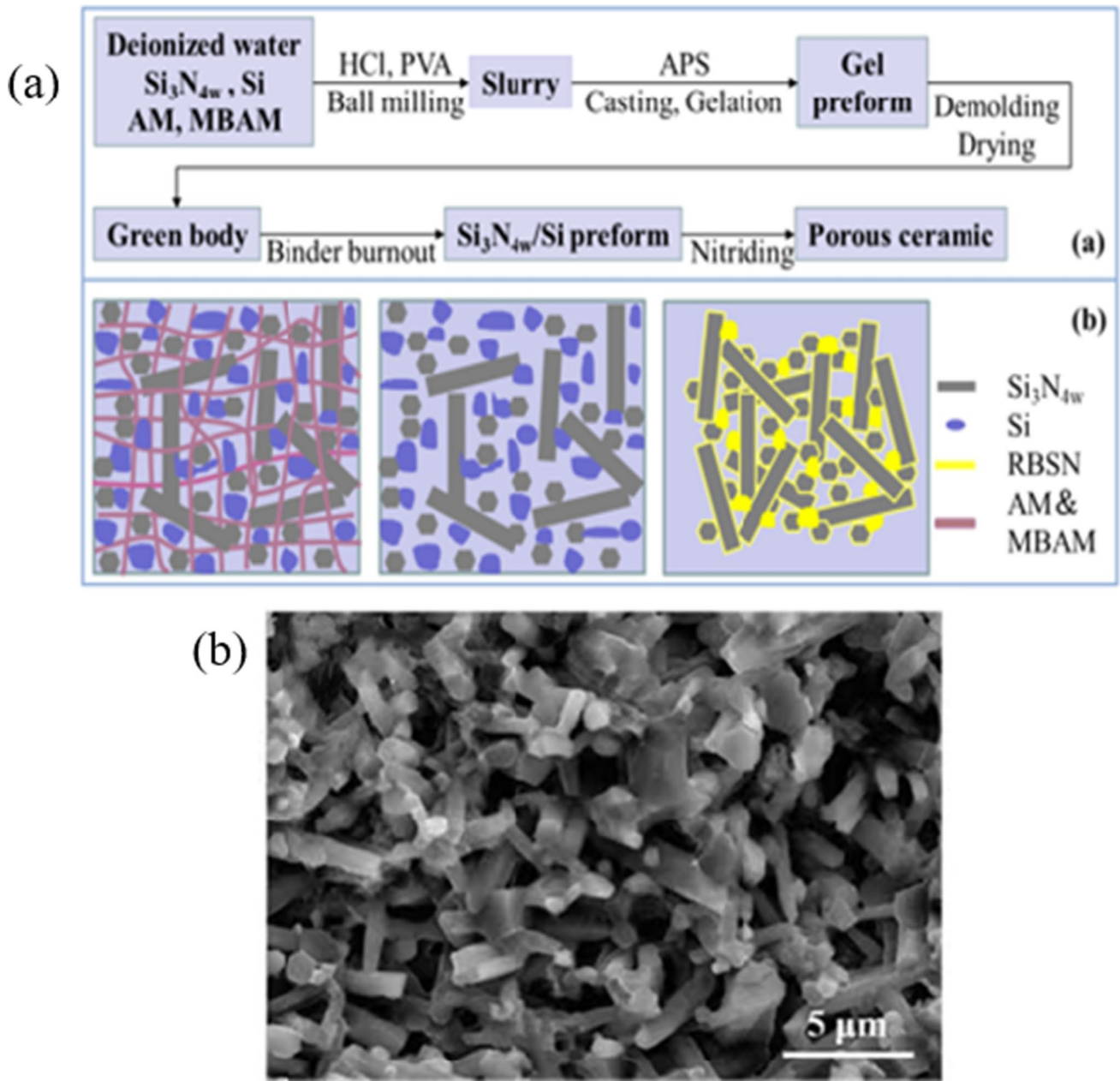


Fig. 14 a Schematic diagram of Gel casting method [19] b the pore morphology of porous Si_3N_4 billet [46]

Table 3 Comparison of dielectric properties of porous silicon nitride with different preparation methods

Methods	The main raw material	porosity /%	Bending strength/MPa	Dielectric constant
Gel casting mold combined with in situ nitriding [19]	$\beta\text{-Si}_3\text{N}_4/\text{Si}=5$	56.7	44.9	2.7
Gel casting mold pressure less sintering [55]	$\alpha\text{-Si}_3\text{N}_4$	39.28	146.0	4.03
Gel casting mold method [36]	$\alpha\text{-Si}_3\text{N}_4$ powder; $\beta\text{-Si}_3\text{N}_4$ seed	41.77	378.5	4.7
Gel casting molding combined with air pressure sintering [34]	$\alpha\text{-Si}_3\text{N}_4$; $\beta\text{-Si}_3\text{N}_4$	36.4~57.6	108.3~235.1	2.63~3.68
Microwave sintering [28]	Si powder	42~78	50~300	2~8
Pore-forming agents, spray drying, and cold isostatic pressing methods [48]	$\alpha\text{-Si}_3\text{N}_4$	51	122	3.46

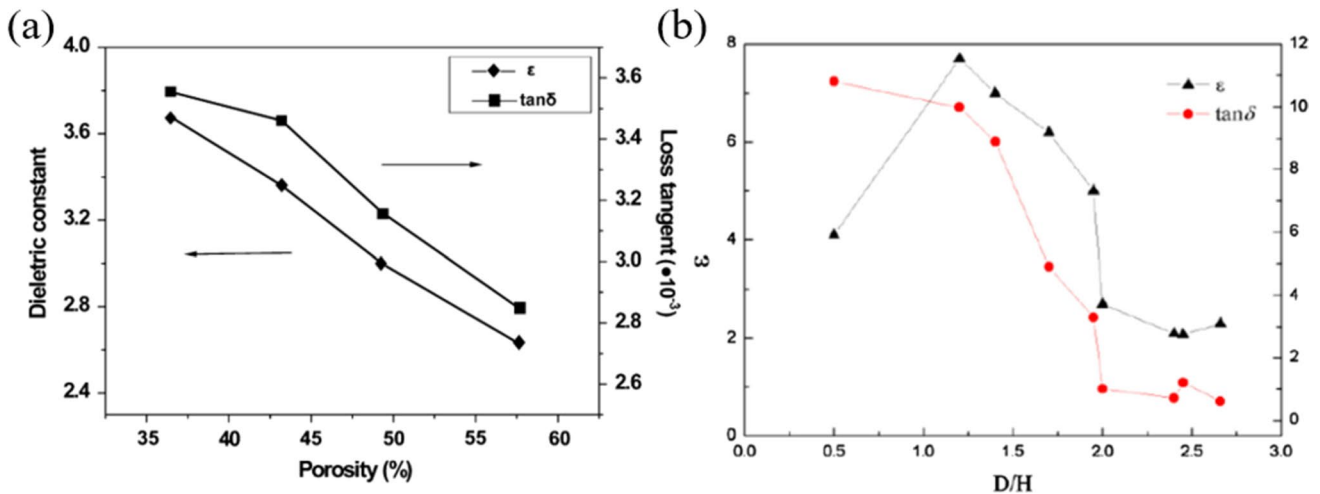


Fig. 15 a Relationship between dielectric constant and loss tangent of porous Si₃N₄ ceramics and porosity[34] b Effect of diameter-thickness ratio on dielectric coefficient [28]

a certain degree of dielectric constant increase, which is related to the increase of material density. Therefore, it is difficult to make a balance between lower dielectric constant and higher thermal stability and mechanical properties of porous silicon nitride ceramics.

3.2 Sound Absorption Properties

The principle of sound absorption of porous ceramics is that sound waves are propagated in porous ceramic pore structures, caused by sound and vibration of the air with porous ceramic hole wall friction. The friction changes the kinetic energy into the heat energy of the air and decreases air vibration energy [67]. Meanwhile, Pores in porous

materials act as resonators, When sound waves diffused into the pore, the waves would reflect once come across the pore walls, resulting in the sound wave resonance. the resonance would push the air in the pore to move forth and back, resulting in a loss of sound energy, the effect is shown in Fig. 17(a) [68]. Thus, the porous ceramics can absorb sound. Sound absorption performance is characterized by the sound absorption coefficient, which is the fraction of incident sound energy absorbed at a given frequency (1000–6500 Hz) [69]. The testing device was schematically shown in Fig. 17(b), the incoming sound waves were generated by a speaker at one end of the tube, while the ceramic foam sample was placed at the other end.

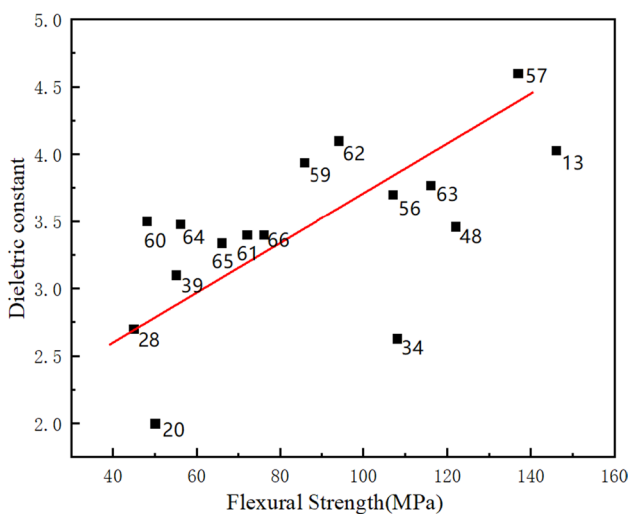


Fig. 16 The dielectric constant and flexural strength of porous Si₃N₄ ceramics in different studies [13, 19, 28, 34, 39, 48, 56–66] MPa

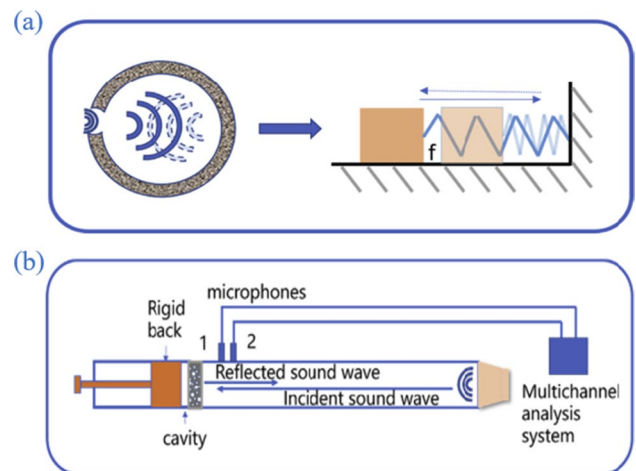


Fig. 17 a Schematic illustration of the single pore resonator and its mechanical analogy of the energy loss [70]. b Schematic diagram of sound absorption testing device of Si₃N₄ceramic foams [70]

Wang et al. [71] investigated the sound absorption performance of Si_3N_4 porous ceramics prepared by the direct foaming method. As shown in Fig. 18(a), the volume of foamed slurries could be controlled by changing the balls' volume. The porosity of porous Si_3N_4 ceramic could be designed by the volume of balls and slurries before foaming. The result was shown in Fig. 18(b), both low-frequency sound absorption (section A) and high-frequency sound absorption (section C) were in direct proportion to porosity of porous ceramics. However, in a middle frequency of around 2200–3100 Hz, porous Si_3N_4 ceramics with 70% designed porosity showed the highest sound absorption coefficient. Pore size should be taken into consideration in this part, which revealed the influence of porosity and average pore size on the broadband sound absorption coefficient.

Du Zhong-pei et al. [70] studied the sound absorption performance of Si_3N_4 porous ceramics with high porosity, and the effect of structural factors such as porosity and pore size on the sound absorption performance of porous ceramics was investigated. The result was shown in Fig. 19. Figure 19(a) showed the sound absorption performance of Si_3N_4 foam ceramics with different average pore sizes and similar porosity. The decrease of the average pore size is beneficial to the improvement of the sound absorption performance of the foam ceramics. This was related to the resonance effect caused by pores. Basically, smaller pores would produce a stronger resonance effect, resulting in better sound absorption. Figure 19(b) showed the sound absorption properties of ceramic foams with different porosity. It could be observed that the higher porosity resulted in a higher sound absorption coefficient. This phenomenon was related to flow resistance,

the increase in porosity reduced the flow resistance, and the lower flow resistance could lead to the easier transfer of sound waves into the ceramic foams. Subsequently, the sound energy was easily dissipated by friction with the pore wall, thus improving the sound absorption performance.

3.3 Permeability

The permeability of ceramics is generally measured by Darcy (K_1) and non-Darcy (K_2) permeability constants. The higher the Darcy (K_1) and non-Darcy (K_2) permeability, the better the permeability. The K_1 is affected by multiple factors, and the specific factors are as follows.

$$k_1 = \frac{\varepsilon d^2}{16f_{ck}\tau^2}$$

Where ε is the effective porosity, d is the average pore diameter, f_{ck} is the Karman-Krosney coefficient and τ is the pore curvature [59]. K_1 value is positively correlated with the effective opening rate, which is directly proportional to the square of the average aperture and inversely proportional to the square of the curvature. K_2 is related to the energy loss caused by the change of flow direction in irregular channels, which is directly affected by the twists and turns of the channel structure. Among them, the larger the bending degree was, the larger the energy consumption and the worse the permeability was. The permeability is related to the porosity. Considering the bending strength, high porosity should be adjusted during the preparation. In order to obtain ceramics with good permeability, the common preparation methods are cold isostatic

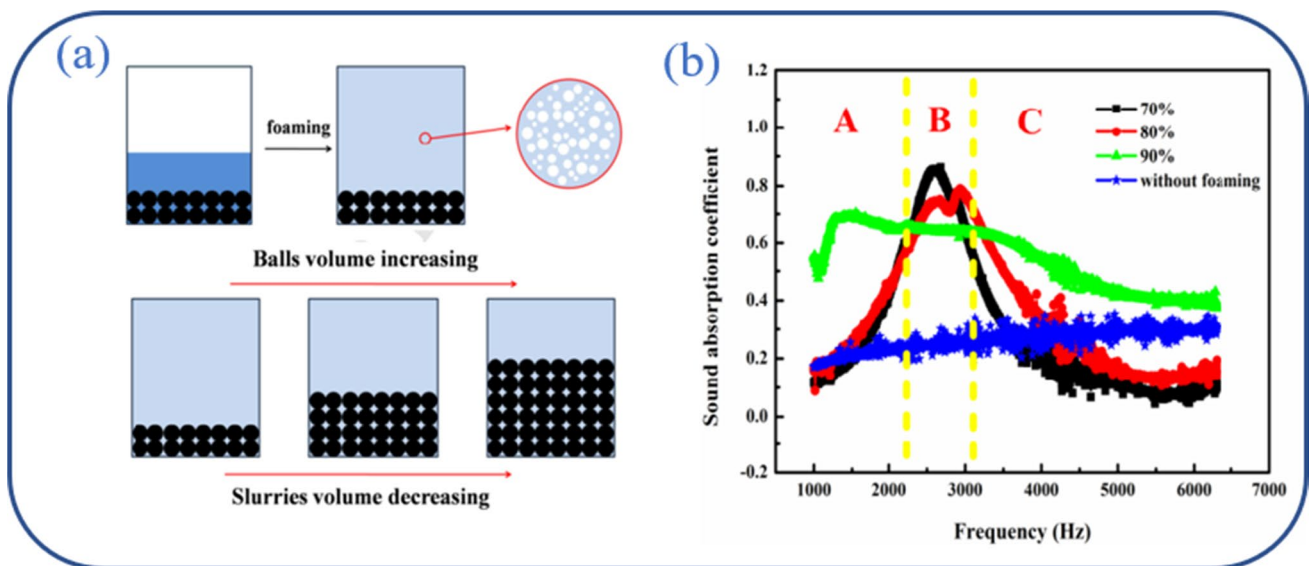


Fig. 18 a Schematic illustration of the volume-controlled foaming procedure [71]; b Sound absorption coefficient of the porous Si_3N_4 ceramics with differently designed porosity [71]

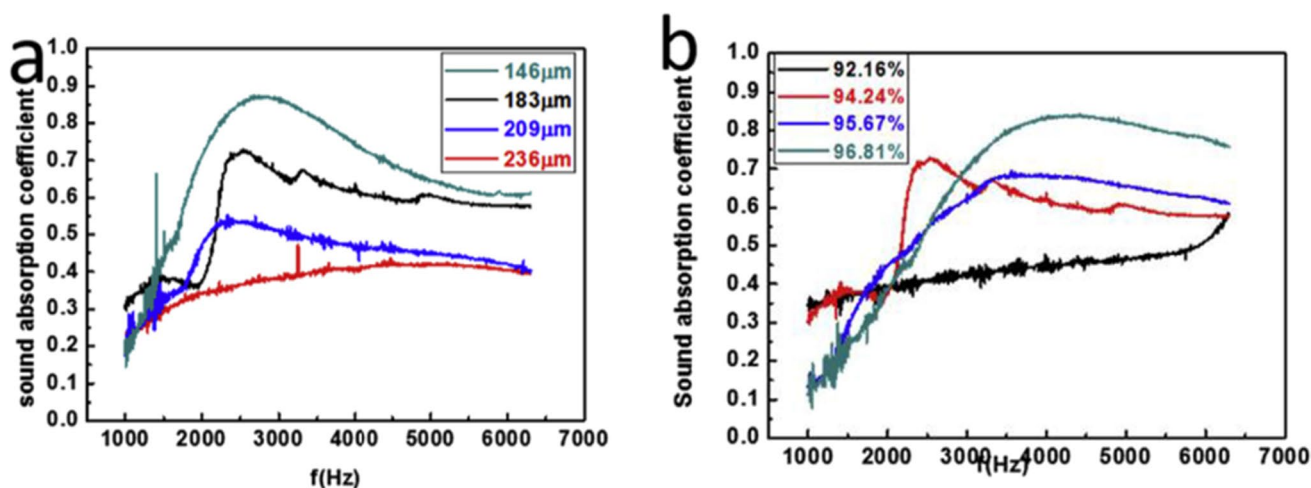


Fig. 19 **a** Sound absorption properties of Si_3N_4 ceramic foams with different pore sizes; **b** Sound absorption properties of Si_3N_4 ceramic foams with different porosity [70]

pressing [53], pore-forming agent [14] and freezing casting [61]. Li et al. [25] prepared porous Si_3N_4 ceramics via cold isostatic pressing without pore-forming agent. Besides, the varied ceramic slurry and emulsified ice template samples were applied to obtain the products with excellent permeability by the freeze casting method. Figure 20 showed the relationship between Darcy (K_1) rate and porosity of the three different preparation processes. The permeability improved with the increase of the porosity. One notes that the Darcy (K_1) and non-Darcy (K_2) permeability of samples obtained by cold isostatic pressing are smaller than that of samples prepared using freeze-casting. This is due to the small porosity and pore size of the ceramics. Moreover, it is worth noting that the emulsion-ice templated samples show smaller Darcy(K_1) permeability compared with ice-templated specimens during

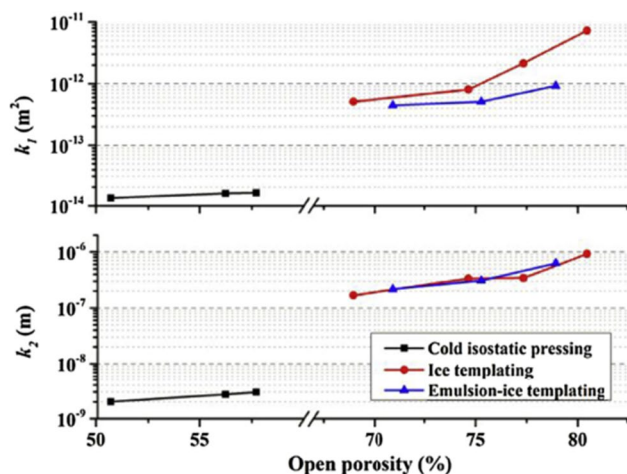


Fig. 20 The dependence of Darcy (K_1) and non-Darcy (K_2) permeability coefficients on open porosity [25]

freeze-casting because of their smaller pore size and higher tortuosity. However, the non-Darcy (K_2) permeability of the sample prepared by emulsion ice templating is similar to that of the sample prepared by ice templating due to their better pore interconnectivity.

Hu et al. [14] applied polymethyl methacrylate (PMMA) as pore forming agent, and prepared Si_3N_4 porous ceramics with a tailored pore structure by self-propagating high-temperature synthesis (SHS). The Darcy (K_1) and non-Darcy (K_2) permeability were even higher than that of the freeze-casting method. It provides a new low-cost method for preparing porous Si_3N_4 carriers with high permeability. Figure 21 illustrates the comparison of the permeability of commonly used porous Si_3N_4 ceramics with other porous ceramics, such as porous aluminosilicate (LAS) ceramics [72], composite ceramics [73], alumina ceramics [74, 75], cordierite bonded porous silicon carbide ceramics [76], polymer derived ceramics (PDC) [77], etc. Meanwhile, the pore-forming agent method, cold isostatic pressing method and freeze-casting method are marked with different color zones. The data was basically distributed around the curve (curve is an empirical formula between K_1 and K_2). It is worthwhile to mention that the obtained porous Si_3N_4 ceramics by freeze casting have better permeability. Owing to its excellent mechanical property, porous Si_3N_4 ceramics with high porosity and large pore sizes has relatively optimal permeability.

4 Application

Porous Si_3N_4 ceramics has the advantages of high specific strength, specific modulus, high thermal conductivity, high-temperature resistance, and thermal shock resistance. In recent years, with the development of technology, the

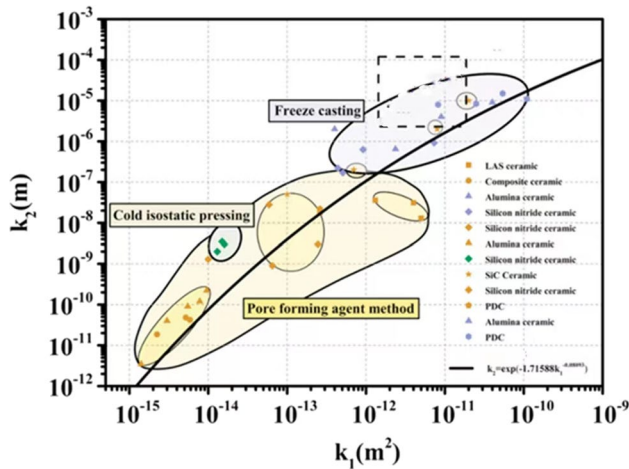


Fig. 21 Comparison of the permeability of common porous Si_3N_4 ceramics prepared with other porous ceramics [14]

stability and reliability of porous silicon nitride ceramics are improved, and its application fields are constantly explored and expanded. As new structural materials and functional materials, the main application fields of the porous silicon nitride ceramics as shown in Fig. 22, include the smelting industry, filter material, radio-transmitting materials, catalyst carrier application, biomedical and sound absorption and noise reduction in extreme environments.

4.1 Smelting Industry Application

Porous silicon nitride ceramics have a low linear expansion coefficient and good thermal shock resistance [78]. It exhibits excellent mechanical strength and electrical insulation, and low creep at high temperatures. Besides, it has excellent chemical properties and corrosion resistance on all inorganic acids except HF solution. At present, in the smelting production line (aluminum smelting, aluminum melting, etc.), porous silicon nitride ceramics are used as thermocouple bushing, substrate panel, crucibles, the pump, pipe for aluminum casting mold conveying high-temperature liquid.

4.2 Filter Material Application

The application of porous Si_3N_4 as filter material mainly focuses on two aspects:

- (1) dusty airflow filter at high temperature or high pressure. Compared with cyclone vacuum cleaners, washing filters, and electric dust collectors, its advantages are high cleaning efficiency and long service life under high pressure [79].

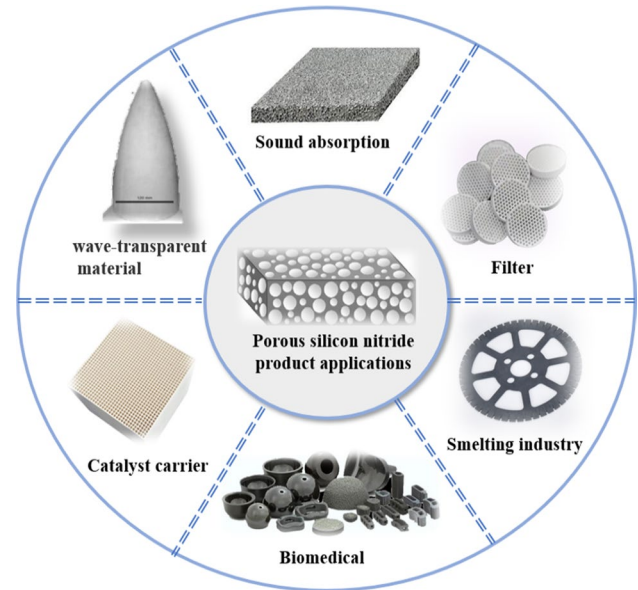


Fig. 22 Application fields of the porous silicon nitride ceramics

- (2) molten metal filter in the foundry industry. Foam Si_3N_4 ceramic filters are used to remove non-metallic inclusions [33]. For this application, the requirements of porous Si_3N_4 ceramics are suggested as follows:

- (i). Do not react with the filtered metal at high temperatures;
- (ii). The filter should have good thermal shock resistance and sufficient strength;
- (iii). It has proper pore size and good permeability, which can not only prevent unnecessary suspended matter from passing through but also make the liquid phase pass through smoothly.

4.3 Wave-transparent Materials Application

The wave-transparent materials (such as radome) used in the aerospace industry should have a lower dielectric loss, stronger erosion resistance, better thermal shock resistance and better mechanical properties [80, 81]. Porous silicon nitride ceramics exhibit great potential in the application of aerospace wave-transmitting materials due to their excellent mechanical properties, broadband transmittance, and stability [13, 82–84]. It is called one of the most promising radome materials and plays an important role in the upgrading of military equipment. The dielectric constant of dense Si_3N_4 ($\epsilon = 7.96\text{--}8.59$) is relatively high when compared with other radome materials, and this drawback would limit its application on the production of thick structural parts of over 5 mm because their overall dielectric constant

should be lower than 6 [55]. Porous ceramics with closed cell structures have low dielectric loss, low density and low absorption rate of radar wave per unit thickness compared with other compact ceramic materials. It is reported that Israel has developed a kind of low-density porous silicon nitride radome material. Its dielectric constant is 2.5–8, and dielectric loss $\tan\delta$ is less than 3×10^{-3} . As mentioned above, the gel casting process is one of the most common methods to prepare excellent dielectric properties at present. Besides, Zhang Xiao-yan et al. [66] used the PVA hydrogel through the freeze–thaw technique innovatively to complete the forming process of porous Si_3N_4 ceramics. After freeze–thaw 2 cycles with the freezing time of 24 h, porous Si_3N_4 ceramics with excellent properties could be prepared, whose flexural strength is 85.72 MPa, the dielectric constant is 3.94 and thermal conductivity is 2.19 W/(m K), providing potential applications in radome materials.

4.4 Catalyst Carrier Application

The application of porous Si_3N_4 as catalyst carrier materials mainly focus on two aspects: (1) chemical catalyst carrier. Most chemical products need to make full use of a catalyst, and the catalyst carrier requires high geometric area and chemical resistance, heat resistance, and corrosion resistance. For example, the most important method for vehicle emission control is the three-way catalysis (TWC) method [85]. The main principle of TWC devices is to use catalysts and purifiers to convert HC, CO and NO_x emitted from automobile exhaust into harmless gases [86]. Porous ceramics are used as a catalyst and purifier carriers because of their advantages such as high surface area, strong adsorption capacity, excellent pore structure, good thermal stability, and low density. Compared with metals, organic porous materials, alumina ceramics and porous cocoon bluestone ceramics, porous silicon nitride ceramics have the advantages of low dielectric constant, resistance to chemical corrosion and catalyst, which can greatly improve the dispersion of catalysts in a hostile environment.

4.5 Biomedical Application

As an inert bio ceramic material, silicon nitride spinal implants have been implanted in the medical field since 1986. In 2006, the US Food and Drug Administration (FDA) officially approved the clinical application of the silicon nitride spinal fusion device produced by America [87]. With the development of biomedical materials research, it is found that silicon nitride ceramics not only have good biocompatibility and bone conductivity but also show good affinity with cells and other biological tissues, which is an ideal human implant material. Most studies have focused on dense

silicon nitride with the aim of replacing metal alloys used in hip and knee prostheses [87–89].

In addition to dense silicon nitride ceramics, porous ceramics have been extensively studied for biological applications. Porous silicon nitride with a cancellous bone-like structure has been commercially used in spinal fusion implants with bone growth rates similar to those reported for porous titanium [90]. Silicon nitride is now emerging as a novel and promising bio ceramic material for a multitude of medical applications. These applications include wear-resistant bearings for knee implants, novel dental implants, spinal intervertebral spacers, tissue engineering scaffolds, antibacterial and antiviral coatings, waveguides for medical diagnostics, microtubes for intelligent neural circuits, micro-spectroscopic imaging devices, photonic ICs, optical biosensors, and others [91, 92]. As an additional bonus, most recently silicon nitride has been found to be a powerful solid-state bio ceramic deactivator of single-stranded RNA (ss-RNA) viruses including the SARS-CoV-2 virus [93]. Anti-microbial kill masks made from silicon nitride-coated polypropylene fibers are being developed commercially to prevent the COVID-19 pandemic. In view of all these beneficial properties, silicon nitride can rightly be considered as close to ideal bio ceramics.

4.6 Sound Absorption and Noise Reduction Application

Noise pollution is one of the serious problems due to the rapid development of the industry. As one of the effective ways of noise reduction, porous sound absorption material has been widely concerned in recent years. Porous absorbent material has the unique properties of lightweight, large specific surface area, and easy molding [94]. Acoustic porous materials can be divided into organic, metallic, and inorganic non-metallic materials by substance. However, the use of most organic and metallic materials in extreme environments such as high temperatures and oil pollution, is limited because of their low thermal and chemical stability. The porous silicon nitride ceramics have good chemical stability, excellent thermal stability and good mechanical properties, which makes it an ideal noise reduction material in some extreme environments [95].

5 Conclusion

5.1 Review of Porous Si_3N_4 Ceramic

In this paper, the preparation, properties and applications of porous silicon nitride ceramics are reviewed as shown in Fig. 23. There are many methods to prepare porous silicon nitride ceramics, including phase change sintering

method, reaction sintering method and carbothermal reduction method according to the difference of initial materials. The advantages and disadvantages of the three methods are described. The porous ceramics prepared by phase change sintering with α - Si_3N_4 as the starting material have a higher flexural strength and better mechanical properties while ensuring the porosity of ceramics. However, the original powder of α - Si_3N_4 has higher price and higher production cost.

According to the way of forming pores, it can be divided into the extrusion forming method, direct foaming method, freezing casting method and gel casting method. The mechanism and preparation process of the four methods were described, their mechanical properties and porosity were compared, and their corresponding application potential was summarized. In terms of performance, the dielectric properties, sound absorption properties and permeability properties of porous Si_3N_4 ceramics were mainly introduced, and the key influencing factors of the three properties and the performance comparison among different preparation methods were described. The outstanding characteristic of porous ceramics in terms of performance is that with the increase of porosity, its dielectric properties, sound

absorption properties and permeability are improved, but its mechanical strength will decrease obviously. How to achieve the comprehensive performance of superior porous ceramics is the key research.

5.2 Technological Evaluation and Outlooks of Porous Si_3N_4 Ceramic

Si_3N_4 porous ceramics have been studied and reported by many scholars, and some progress and achievements have been made, but there are still some problems that need to be further studied.

Firstly, in the preparation of high-performance ceramics, the safety of the human body should be ensured and the harm to the environment should be reduced. For example, gel casting molding as an advanced near-net forming process, has attracted extensive attention in the preparation of high-strength porous silicon nitride ceramics. However, in the preparation process, acrylamide (AM) containing neurotoxin is still the most widely used monomer in gel casting molding because of its high billet strength., which poses a serious threat to human health and the environment because of its high billet strength. So far, many non-toxic natural

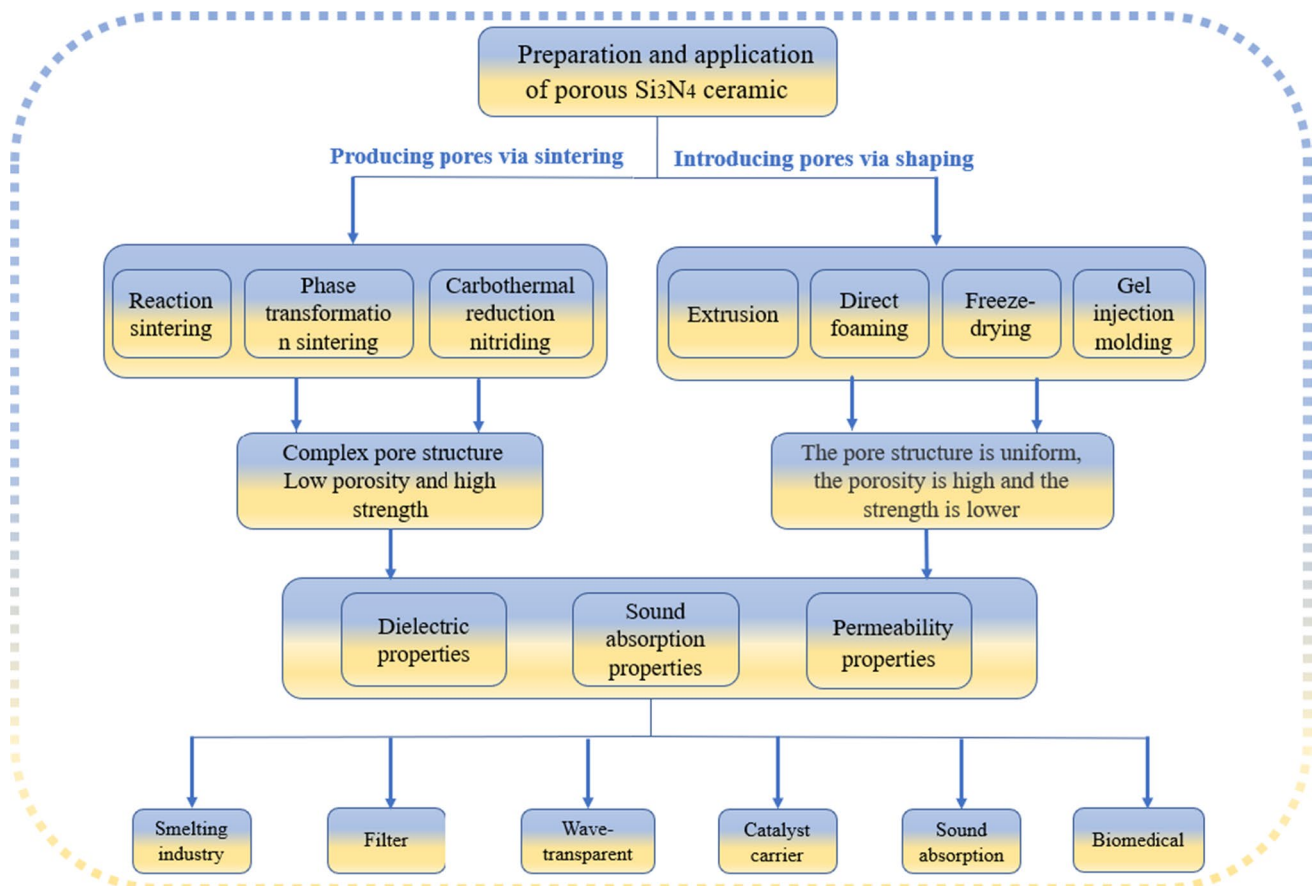


Fig. 23 General framework of the article

substances, including agarose, starch, chitosan, some low-toxicity monomers, including 2-hydroxyethyl methacrylate (HEMA), methacrylamide (MAM), N-methylol acrylamide (NMAM), N-dimethylacrylamide (DMAA), etc., have also been rapidly developed in the gel molding of many ceramics. There is still a long way to go to develop gel systems with low toxicity or non-toxicity to replace AM systems.

Secondly, the process parameters should be carefully controlled to control the microstructure and properties in the process of ceramic preparation, so as to improve the porosity and ensure its strength. Further research is needed to reveal the essential relationship between the microstructure and the properties of porous ceramics. The contradictory balance between current strength and porosity (wave permeability and dielectric properties), surface area (load capacity) and pore size (permeability) are always the bottleneck restricting the performance and application of porous silicon nitride ceramics. There are many solutions. For example, in the preparation of porous Si_3N_4 ceramics adding a small amount of carbon and sintering additives to Si_3N_4 ceramics, reaction-induced phase separation can be used to prepare Si_3N_4 ceramics with high porosity. The overall strength of ceramics is improved by introducing a second phase of the nailed boundary to inhibit volume shrinkage. At the same time, fine crystal Si_3N_4 ceramics, especially nanoscale Si_3N_4 ceramics, are expected to show excellent mechanical properties, and the preparation of high porosity Si_3N_4 bulk ceramics with excellent strength of fibrous particles is also worth exploring.

Furthermore, the cost can be significantly reduced by using cheaper raw materials or reducing the sintering temperature or simplifying the sintering process. For example, some scholars have prepared porous Si_3N_4 ceramics by low-temperature pressure-free sintering using carbonized rice husk and $\alpha\text{-Si}_3\text{N}_4$ powder as raw materials. In addition, Combustion synthesis (SHS) has attracted much attention because of its unique advantages of energy saving and high purity of products. However, the sintering shrinkage characteristics and dimensional stability mechanism of porous Si_3N_4 ceramics synthesized by self-propagation remain to be studied.

Finally, porous silicon nitride composite is also a research hotspot to improve its comprehensive properties and seek wider applications. For example, $\text{Si}_3\text{N}_4/\text{Al}$ two-phase continuous composites were prepared with porous ceramic Si_3N_4 and Al-Si₁₂ alloy as matrix, which greatly improved the fracture toughness. Some scholars have reduced the thermal conductivity by adding lightweight thermal insulation materials as fillers to the large pores to form mesoporous structures, that is, using $\text{ZrO}_2\text{-SiO}_2$ aerogels as fillers to improve the thermal insulation performance and stability of fiber ceramics. It also provides a new direction for the

preparation of silicon nitride ceramics in the future. Due to the excellent properties and application potential of porous Si_3N_4 , applications in other fields should be studied and reported more.

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Declarations

Consent to Publish All the authors have agreed to publish.

Consent to Participate All the authors have agreed to participate.

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