

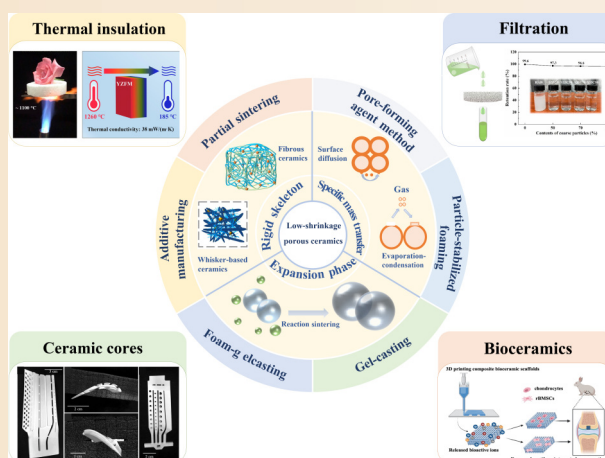
Low sintering shrinkage porous ceramics: Principles, progress, and perspectives

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ABSTRACT: Porous ceramics are lightweight materials with diverse pore structures and are widely applied in areas such as thermal insulation, sound absorption, filtration, catalysis, and energy storage. However, excessive shrinkage during the sintering process of porous ceramics leads to cracking and deterioration, posing significant challenges for achieving complex shapes. Despite its importance, the field of low sintering shrinkage porous ceramics has not received sufficient attention. This review systematically discusses the principles and progress in the development of low sintering shrinkage porous ceramics. First, we introduce the characteristics of various preparation methods, including partial sintering, particle-stabilized foaming, gel-casting, foam-gelcasting, and additive manufacturing (AM). We then explain three primary principles of low sintering shrinkage from the perspectives of the volume effect and mass transfer processes. This review focuses on the properties and applications of typical low sintering shrinkage ceramics such as mullite and alumina, particularly their mechanical properties and thermal conductivity as thermal insulation and ceramic cores. Finally, we summarize the current state and present future perspectives on low sintering shrinkage porous ceramics.

KEYWORDS: porous ceramics; low sintering shrinkage; volume expansion; mass transfer process; pore structure; properties



1 Introduction

Porous ceramics exhibit special structures and are recognized for their lightweight properties, high specific surface area, excellent corrosion and heat resistance, and thermodynamic stability performance [1]. As recommended by the International Union of Pure and Applied Chemistry (IUPAC), porous materials can be classified into three types on the basis of their pore size: microporous (< 2 nm), mesoporous (2–50 nm), and macroporous (> 50 nm) [2]. Porous structures can be divided into closed and open pores, while open pores include connected pores and discrete pores with one side closed. Owing to their different structures and properties, such as pore size, distribution, and connectivity, porous ceramics are broadly used in diverse fields, such as filtration [3,4], absorption [5,6], catalyst support [7,8], thermal insulation [9–11], and biomedical implants [12]. Moreover, the pore structure is strongly related to the processing method. The fabrication methods for porous ceramics include

partial sintering [13], the pore-forming agent method [14,15], particle-stabilized foaming [16], gel-casting [17–19], foam-gelcasting [20–22], additive manufacturing (AM) [23–25], etc. By changing or combining process methods, porous ceramics with a wide range of pore distributions and various structures can be produced. A schematic diagram of the fabrication methods, the pore structure, and potential applications of porous ceramics is shown in Fig. 1.

However, deformation and cracking caused by large sintering shrinkage usually occur during the sintering process and limit the dimensional accuracy of porous ceramics. Low sintering shrinkage indicates that the dimensional changes in the materials are minimal during the sintering process, which helps to maintain the structural stability of ceramics and ensures the accuracy and consistency of the products [32,33]. Additionally, the need for subsequent machining and adjustments is reduced, further decreasing the production costs. Moreover, low shrinkage contributes to maintaining the uniformity and connectivity of the

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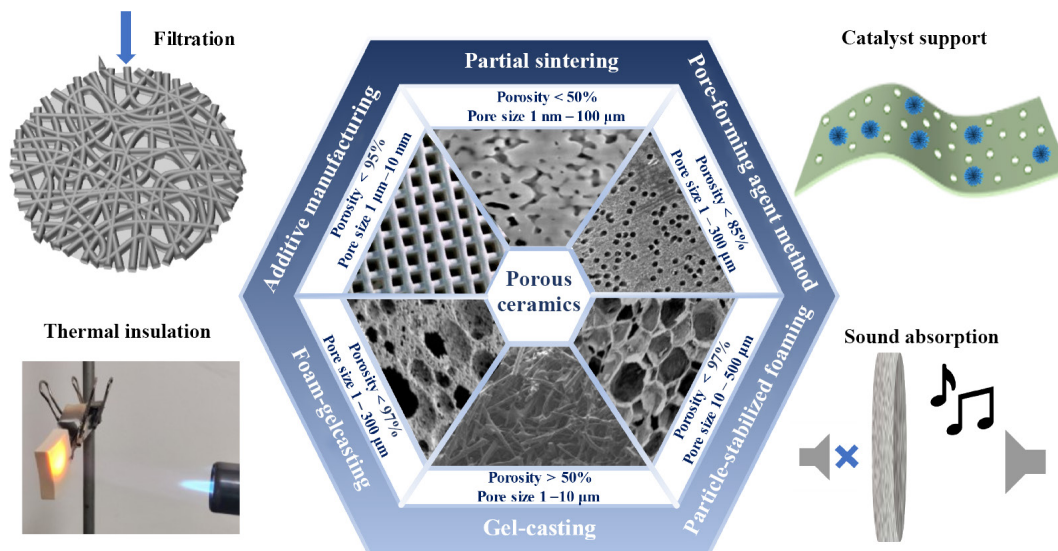


Fig. 1 Schematic diagram of fabrication methods, pore structure, and potential applications of porous ceramics. The image of partial sintering is reproduced with permission from Ref. [26], © Elsevier Ltd. 2013. An image of pore-forming agent method is reproduced with permission from Ref. [27], © Elsevier Ltd. 2005. An image of particle-stabilized foam is reproduced with permission from Ref. [28], © Elsevier Ltd. 2013. Image of gel-casting is reproduced with permission from Ref. [29], © Elsevier Ltd and Techna Group S.r.l. 2016. Image of foam-gelcasting is reproduced with permission from Ref. [30], © Elsevier Ltd. and Techna Group S.r.l. 2022. Image of the additive manufacturing is reproduced with permission from Ref. [31], © Elsevier Ltd. 2020.

porous structure, thereby enhancing the functionality of the ceramics. Conversely, excessive sintering shrinkage results in a high waste rate and low production efficiency. Hence, to achieve complex shaping, low sintering shrinkage porous ceramics have been gradually proposed.

Recently, several reviews focusing on porous ceramics have been reported. Colombo [34], Studart *et al.* [35], and Ohji and Fukushima [36] reviewed the processing routes of macroporous ceramics. Hammel *et al.* [37] reviewed the applications and processing of advanced porous ceramics, whereas Vakifahmetoglu *et al.* [38] focused on porous polymer-derived ceramics (PDCs). Nishihara *et al.* [39] concentrated on porous ceramics made by tape casting, whereas Hwa *et al.* [40] and Zhang *et al.* [41] focused on the fabrication and applications of three-dimensional (3D)-printed porous ceramics. Chen *et al.* [42] studied porous ceramics with large porosities and pore size distributions and their contributions to energy and environmental technologies. Nevertheless, there are few systematic comments about low sintering shrinkage porous ceramics. Thus, a review concentrated on low sintering shrinkage porous ceramics could fill this gap by providing a comprehensive analysis of the characteristics, production processes, and application domains, which would offer a theoretical foundation and guidance for further optimization and exploration of new applications in porous ceramics, thereby stimulating the generation of novel research perspectives. This approach holds significant importance for the industrial production and application of low sintering shrinkage porous ceramics, enhancing the sustainable development of the industry.

In this review, we define low sintering shrinkage porous ceramics as those whose shrinkage is less than 10%, and porosity is greater than 30% and then expound upon the fabrication methods and low sintering shrinkage principles of porous ceramics combined with different material categories. Specifically, this review focuses on reducing sintering shrinkage, provides a synthesis of porous ceramics conducive to near-net-size manufacturing, and proposes a perspective on advancements in low sintering shrinkage porous ceramics concerning their mechanical and thermal properties and potential applications.

2 Processing of porous ceramics

2.1 Partial sintering

Compared with complete densification sintering, partial sintering is a relative concept in which dense ceramics cannot be produced at lower temperatures with shorter processing times to maintain residual porous structures of green bodies and create smaller grains [43]. Typically, the porosities of porous materials created via partial sintering are less than 50%, whereas the pore distributions are narrow [44]. To increase porosity, partial sintering can be combined with slip casting and other forming processes [45]. Table 1 provides a summary of the pore features of the porous ceramics produced via partial sintering. According to classical sintering theory, the factors of densification include the heating rate [46], sintering temperature [47], raw particle properties [48], forming pressure [13], and sintering additives [45]. These factors affect the porosity and pore size of porous ceramics by limiting grain growth and densification.

The sintering temperature and forming pressure impact the microstructures of the final products directly. A high sintering temperature leads to sufficient mass transfer processes and grain growth with decreased porosity, whereas a low forming pressure results in the agglomeration of fine material grains and localized nonuniform shrinkage of porous ceramics. Deng *et al.* [13] sintered nano zirconia powders (average grain size of 28 nm) at 1100–1450 °C for 0.5 h with different uniaxial forming pressures (30 and 75 MPa) to obtain ceramics with porosities ranging from 55% to 0%. Nečina *et al.* [48] sintered submicron alumina powders and nanocrystalline zirconia at 1100–1400 °C for 2 h to obtain porous ceramics. The results showed that as the sintering temperature increased, sintering necks formed and strengthened, leading to grain growth and a reduction in porosity. The pores were formed by loose accumulation of grains, and smaller particles resulted in greater densification. Thus, nano zirconia was less porous than submicron alumina when the sintering temperature was increased. Additionally, the wide particle distribution and slow heating rate impact porosity in the same way, promoting mass diffusion and grain growth to reduce porosity.

Sintering additives have a complex effect on material systems, influencing porosity and pore distribution by impacting liquid sintering and mass transfer. A higher forming pressure results in a lower porosity in the green samples and final products. Fukushima *et al.* [49] used β -SiC powders to prepare porous SiC ceramics via cold isostatic pressing (CIP) at various temperatures, pressures, and alumina contents. A lower CIP pressure and sintering temperature increased the porosity in samples with 2 and 4 wt% alumina, although the porosity changes were nonlinear. At 1800 °C, the samples had narrow pore distributions (0.1–1 μm), and the pore size decreased with more alumina, as the oxide liquid limited particle rearrangement, promoting the formation of finer grains.

Figure 2 illustrates the factors influencing partial sintering and shows the typical pore structure of the resulting products. In conclusion, the pore-forming mechanism of partial sintering is incomplete densification, which could also reduce the degree of sintering shrinkage due to insufficient mass transfer. All factors of sintering densification are related to this method; therefore, it is difficult to control the porosity accurately through partial sintering.

2.2 Pore-forming agent method

The pore-forming agent method is a common and economical method for producing porous ceramics. This method involves the

Table 1 Summary of pore features of porous ceramics produced via partial sintering

Material	Sintering temperature (°C)	Uniaxial forming pressure (MPa)	Sintering pressure (MPa)	Porosity (%)	Ref.
SiC	1500–1800	100/400 (CIP)	—	35–45	[49]
Si ₃ N ₄	1600/1800	10	0.5 (N ₂)	15–60	[51]
ZrO ₂	1200/1400	30	Pressureless	47.4/11.8	[13]
	1200/1350	75	Pressureless	44.5/14.6	[13]
	1100–1400	50	Pressureless	3.1–48.6	[48]
Al ₂ O ₃	500–1400	—	Pressureless	0–39.5	[47]
	1000–1300	—	5.5 (vacuum)	30–50	[54]
	1100–1400	200	Pressureless	13.3–40.8	[48]
	1200/1600	—	1.3	56/33	[46]
	1000 (SPS)	—	4–10	52–58	[46]
9PHEB	1500–1750	—	—	30–60	[52]
YB ₄	1780	—	—	60.9–69.6	[53]

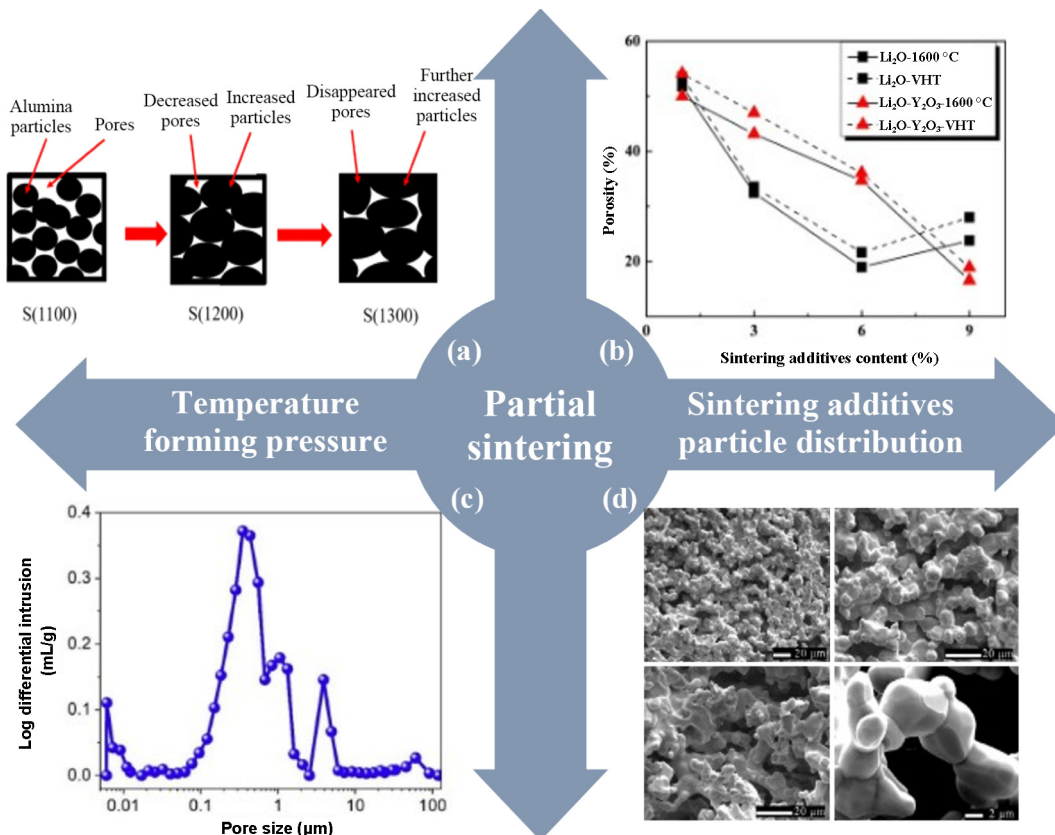


Fig. 2 (a) Schematic of the partial sintering method. Reproduced with permission from Ref. [50], © Elsevier 2019. Typical pore structure of the resulting products: (b) porosity of the porous Si₃N₄ ceramics after sintering at 1600 °C and after vacuum heat treatment (VHT) at 1500 °C with different sintering additives. Reproduced with permission from Ref. [51], © The American Ceramic Society 2014. (c) Pore distribution of porous high-entropy (Hf_{1/9}Zr_{1/9}Ta_{1/9}Nb_{1/9}Ti_{1/9}Cr_{1/9}Mo_{1/9}V_{1/9}W_{1/9})B₂ (9PHEB) ceramics sintered below 2000 °C. Reproduced with permission from Ref. [52], © Wiley-VCH GmbH. 2024. (d) SEM images of porous YB₄ ceramics sintered at 1780 °C. Reproduced with permission from Ref. [53], © Elsevier Ltd. 2015.

incorporation of pore-forming agents, usually during the mixing of raw powders or preparation of suspensions, utilizing their occupied space as the pore source, followed by formation, drying, and sintering to obtain porous ceramics. The basic feature of pore-forming agents is that they can burn out or decompose during sintering to obtain porous structures; thus, the morphology, content, and particle size distribution of pore-forming agents affect the porosity, pore morphology, and pore size distribution of the final porous ceramics. Table 2 provides a summary of the pore features of porous ceramics produced by different pore-forming agents. Pore-forming agents can be divided into organic agents such as nylon fibers [27], starch [55], and polymethylmethacrylate (PMMA) [56] and inorganic agents such as carbon black [57] and H_3PO_4 [58]. Pore size is highly related to agent size and expands with increasing pore-forming agent size [59–61]. Nevertheless, the aggregation and uneven distribution of agents lead to nonuniform pore structures, resulting in poor mechanical properties [62]. A backward feature of this method is that the porosity of the samples typically remains below 80%, owing to the limited distribution of agents.

In general, the pore size and porosity increase with increasing pore-forming agents, which is attributable to the generation of an additional gas phase or the agglomeration of large particles. Liu *et al.* [57] investigated the impact of carbon black as a pore-forming agent on the pore structure of alumina porous ceramics and reported that as the porosity increased, and the nonlinear trend of the volume of pores below 2 μm decreased, whereas those above 14 μm increased with increasing carbon black content, indicating nonuniform aggregation of the agents. The

microstructure of porous ceramics is related to the shape of the pore-forming agent. Isobe *et al.* [27] used nylon fibers to obtain cylindrical pores, whereas Zhou *et al.* [56] used PMMA microspheres to obtain spherical pores. The pore-forming agent is the most critical factor influencing this technique, with its particle size, shape, and relative content directly determining the porosity and pore structure of the samples.

2.3 Particle-stabilized foaming

In the direct foaming method, air bubbles are incorporated into a suspension containing ceramic particles, where surfactants or partially hydrophobic colloidal particles act as interface stabilizers to inhibit the instable behaviors of wet foams to decrease free energy, such as Ostwald ripening and coalescence processes [35]. Compared with ordinary surfactants, partially hydrophobic colloidal particles after modification possess 10^3 – 10^6 times greater attachment energy for adsorption at the gas-liquid interface, endowing them with irreversible adsorption and ultrastable foams for weeks or even longer and avoiding additional setting processes to retain the pore structure [63–65]. That is, particle-stabilized foaming is a direct foaming method based on *in situ* hydrophobization of colloidal particles via surfactants, which can effectively adjust or retain the pore structure of ultrastable foams [66]. In Table 3, the pore features of porous ceramics made by particle-stabilized foaming are summarized, and the applicable material systems are extensive, including metal oxides [67], silica [68], and high-entropy niobates [69]. Surfactants can be categorized into cationic surfactants such as dodecyl trimethyl ammonium chloride (DTAC) [70]; anionic surfactants such as

Table 2 Summary of pore features of porous ceramics produced by different pore-forming agents

Material	Pore-forming agent	Agent size (μm)	Porosity (%)	Pore size (μm)	Ref.
Al_2O_3	Starch	—	6–47	—	[55]
	Nylon fiber	19 (diameter)	20–40	~16	[27]
	Carbon black	0.05–0.10	33.1–68.9	0.5–24	[57]
	Corn cob	63–250	41.3–68.1	37.7–236	[59]
	Waste coffee ground	< 250	35.4–53.8	1–250	[60]
Al_2O_3 -mullite	Carbonized rice husk	~50	25–85	0.99–36.49	[61]
ZrO_2	Yttrium nitrate and magnesium compound	—	36.7–45.4	5–251	[62]
Si_3N_4	PMMA	2–20	43.59–57.34	—	[56]
	H_3PO_4	—	42–63	—	[58]

Table 3 Summary of pore features of porous ceramics produced via particle-stabilized foaming method

Material	Surfactant	Additive	Porosity (%)	Pore size (μm)	Ref.
Hydroxyapatite	PG	—	66–85	—	[80]
Barium strontium titanate (BST)	PG and SDS	—	84.1–94.8	46.4–100.4	[76]
ZrO_2	SDS	—	96–98	—	[71]
Al_2O_3	Propionic acid	—	72	—	[68]
	Propionic acid, butyric acid, and valeric acid	—	40–70	—	[79]
	DTAC	Dispersant: ammonium polyacrylate (PAA)	80–86	64–162	[70]
	DTAC	Dispersant: PAA	77.4–87.9	50–211	[77]
	TLS	—	65.4–69.6	44–51	[78]
ZrO_4 - TiO_2	PG	Binder: polyethyl glycol	57.55–78.33	53.77–101.30	[72]
SiC	Octylamine	Binder: polyethyl glycol	—	~360	[73]
Al_2O_3 - ZrO_2	SDS	—	95.82–96.70	—	[67]
	Valeric acid	—	88–94	80–200	[28]
$(\text{Dy}_{0.2}\text{Ho}_{0.2}\text{Y}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2})_3\text{NbO}_7$	TLS	—	90.13–96.13	20–200	[69]
$(\text{La}_{0.2}\text{Nd}_{0.2}\text{Sm}_{0.2}\text{Gd}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$	TLS	—	87.99–96.89	20–140	[81]

sodium dodecyl sulfate (SDS) [71]; and amphiphilic molecules such as propyl gallate (PG) [72] and octylamine [73] on the basis of their molecular structures, yet their modification effects on colloidal particles are similar. Typically, surface modification of ceramic particles can be realized via a one-step process. Namely, ceramic particles are mixed with a surfactant-containing solution, and then mechanical agitation is conducted to introduce air bubbles, followed by casting, drying, and sintering. Figure 3(a)

illustrates the process of the particle-stabilized foaming technique. The pore morphology, porosity, and pore size distribution are influenced by the type of hydrophobic modifier, hydrophobicity of the particles, solid content, stirring time, and speed, but are minimally correlated with the raw materials [67,71]. The porosity can reach 99%, and a pore size of approximately several hundred micrometers can be created by high-speed mechanical agitation.

Wet foams are thermodynamically unstable because of their

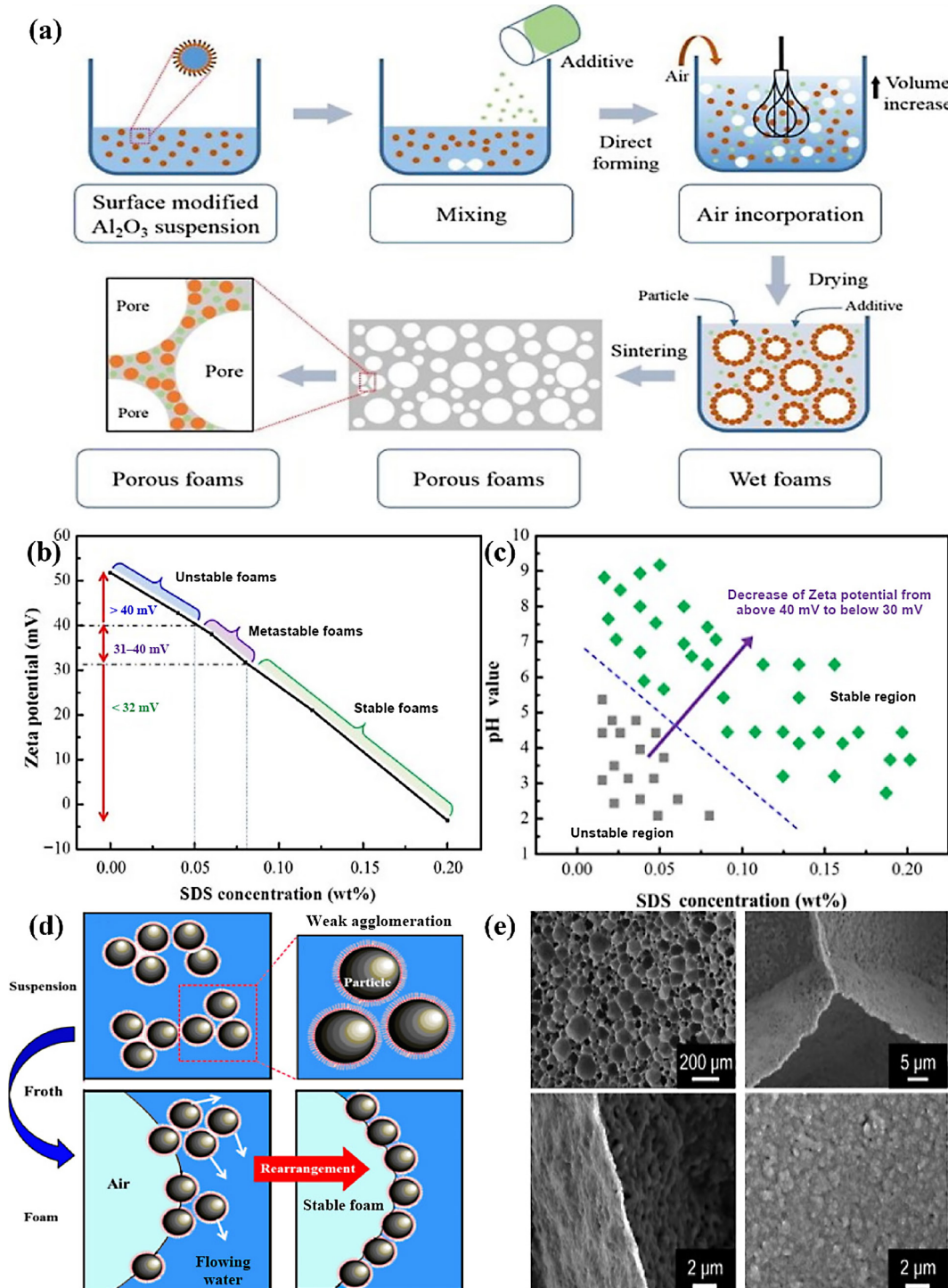


Fig. 3 (a) Schematic diagram of particle-stabilized foaming technique. Reproduced with permission from Ref. [79], © Elsevier Ltd and Techna Group S.r.l. 2014. (b) Stability of alumina ceramic foams fabricated with different SDS concentrations at pH = 4.3. (c) Stability of alumina ceramic foams fabricated with different SDS concentrations and pH values (the green points indicate foams with zeta potentials below 30 mV, whereas the gray points indicate foams with zeta potentials exceeding 30 mV). (d) Schematic of the particle state in the suspension prepared at the IEP during the foaming process. Reproduced with permission from Ref. [75], © Elsevier Ltd. 2018. (e) SEM images of zirconia foams obtained at pH = 7.8 and sintered at 1400 °C. Reproduced with permission from Ref. [71], © The American Ceramic Society 2016.

high gas-liquid interfacial energy. To decrease the overall system free energy, wet foams undergo Ostwald ripening to destabilize and lead to large pores [35]. The critical issue of this method is the stability of high-volume foams in obtaining porous ceramics with ultrahigh porosities. Vivaldini *et al.* [74] commented on the reason for the instability of foams containing colloidal hydrophilic particles and used a ratio of adsorption energy and thermal energy to describe the stability of the gas-liquid interface as Eq. (1) and then proved that the ratio must be at least a few hundred to allow foam stabilization.

$$\text{Interface stability} = \frac{\Delta G_{\text{ads}}}{K_{\text{B}}T} = \frac{\pi\gamma(1 \pm \cos\theta)R_{\text{p}}^2}{K_{\text{B}}T} \quad (1)$$

where ΔG_{ads} is the energy decrease due to the adsorption process at a flat interface, γ is the gas-liquid interfacial tension, θ is the particle contact angle with liquid, R_{p} is the particle radius, K_{B} is the Boltzmann constant, and T is the absolute temperature. When $0^\circ \leq \theta \leq 90^\circ$, the positive sign in Eq. (1) or the negative sign for $\theta > 90^\circ$ is used.

The gas-liquid interfacial tension and contact angle are the most critical factors for assessing the generation and stability of ceramic foams, and the zeta potential can be used to measure the stability of colloidal systems. To adjust these factors, the pH range of slurries and surfactant contents should be considered. By tailoring the pH value and surfactant, Huo *et al.* [75] explored the effects of the zeta potential on the properties of a foam colloidal suspension and revealed the best zeta potential range for foam stability. Figures 3(b) and 3(c) show the stability of alumina ceramic foams under different zeta potentials. Huo *et al.* [76] investigated various contact angles with respect to pH and SDS content and reported that stable foams can be obtained at a suitable pH. Figure 3(d) shows a schematic of the particle state in the colloidal suspension prepared at the isoelectric point (IEP) during the foaming process. As shown in Fig. 3(e), Huo *et al.* [71] produced zirconia ceramic foams with a porosity of 97.9% around IEPs, and the foam walls were even and thin to 0.49 μm without particle aggregation, which means that the foams were stable at this pH value. This demonstrated that a low zeta potential is beneficial for foam stability and that an absolute value of 30–40 mV is the boundary between stable and unstable foams. Research has shown that foam ceramics should be prepared at the IEP using long-chain surfactants to obtain stable and uniform foams with thin and homogeneous walls without agglomeration. Using an anionic dispersant, ammonium polyacrylate, and a cationic surfactant, DTAC, to fix ceramic particles without extra additives, Zhao *et al.* [77] fabricated porous alumina ceramics with porosities ranging from 77.4% to 87.9% and compressive strengths ranging from 5.1 to 37.9 MPa. Wang *et al.* [70] prepared porous alumina ceramics with porosities ranging from 80% to 86% (closed porosities ranging from 11% to 75%) and compressive strengths ranging from 18.5 to 39.0 MPa. Compared with that of the open-cell ceramic foams, the compressive strength of the closed-cell ceramic foams is much greater. Zhao *et al.* [78] produced porous alumina ceramics with highly similar porosities (total porosities ranging from 65.4% to 69.6% and ratios of closed porosity to total porosity ranging from 91.5% to 94.1%) by optimizing the concentration of the surfactant triethanolamine lauryl sulfate (TLS), which results in a high compressive strength ranging from 90 to 128 MPa. This series of studies provides novel ideas for enhancing the mechanical properties of samples prepared by particle-stabilized foaming by improving the closed porosity and observing the influence of the surfactant content on the pore size, indicating that a higher hydrophobic agent content

leads to smaller and more uniform window sizes, resulting in better mechanical strength.

Particle-stabilized foaming is a simple method to produce high-porosity ceramics with even spherical or polyhedral pores, but the main issue lies in the ultrahigh porosity, which reduces their strength.

2.4 Gel-casting

Gel-casting is a method of ceramic slip casting developed by America Oak Ridge National Laboratory to achieve the formation of large and complex shapes [82]. In this method, raw powders, solvents, organic monomers, initiators, and other additives are prepared into a premix solution, followed by molding, gelation, and solidification. Ceramic powders *in situ* form a three-dimensional gel network. It combines a traditional ceramic casting process with the polymerization of organic monomers to obtain uniformly structured green bodies, and then porous ceramics can be obtained by the removal of organics. In particular, gel-casting is suitable for the fabrication of fibrous ceramics [83–85]. Hence, the occupancy of organic matter in the green body determines the pore structure of porous ceramics, and the influencing factors include the type and content of monomers, cross-linking agent, and solvent, as well as the sintering behavior of the raw powders.

The commonly used gelling systems, as well as their pore features and microstructures, are summarized in Table 4. On the basis of the different solvents used, gel-casting methods can be divided into aqueous methods [86], tert-butyl alcohol (TBA)-based methods [87], etc. Acrylamide (AM) and N,N'-methylene bisacrylamide (MBAM) are widely applied for gelation because of their stable polymerization in various solvents [88,89], whereas some gelling sources are chosen because of their hydrolysis, such as hydrocarbon alumina ($\rho\text{-Al}_2\text{O}_3$) [90]. Figure 4 shows three common gel-casting systems that can be used to fabricate porous ceramics with different microstructures. The solid loadings are less than 50%, whereas a high loading content leads to a high viscosity and inhomogeneous dispersion of the slurry, restricting the integrity of green body formation [91]. Owing to the addition of gelation, the thick slurry impedes the generation and expansion of pores, causing the porosity to be approximately 70% and the average pore size to be under 10 μm .

Solvents have a strong influence on gelling behavior. Jin *et al.* [88] explored the gelation behaviors of AM and MBAM in water, TBA, and ethylene glycol (EG). Figure 5 shows that the dispersants critically impact the microstructures of the products, indicating that the precipitation polymerization of AM/MBAM formed in TBA produced small gel particles and thin gel walls, while the solution polymerization occurred in water and that EG generated continuous and thick gel walls with high strength. Using the EG-based gel-casting process, Jin *et al.* [88] prepared porous SiC ceramics with a porosity of 74.1% and an average pore diameter of 3.48 μm . The sharp single peak distribution indicates the uniform pore structure of the samples created via gel-casting. Using the TBA-based gel-casting process, Hou *et al.* [94] prepared Y_2SiO_5 porous ceramics with porosities ranging from 66.70% to 50.01%, compressive strengths ranging from 3.43 to 24.45 MPa, and thermal conductivities ranging from 0.08 to 0.55 W/(m·K). Without toxic TBA, aqueous gel-casting is an eco-friendly method that uses inorganic or less organic compounds that undergo hydration or gelation reactions as gelling agents to achieve the formation of a network structure. Using $\rho\text{-Al}_2\text{O}_3$ as the gelling source instead of organics that emit greenhouse gases upon combustion, Yuan *et al.* [84] obtained fibrous Al_2O_3 -YSZ porous ceramics with porosities ranging from 71.1% to 72.7%,

Table 4 Summary of pore features of porous ceramics produced via gel-casting method

Material	Solvent	Solid loading	Organic monomer	Crosslinking agents/gelling source	Porosity (%)	Average pore size (μm)	Ref.
Mullite	Deionized water	—	—	$\rho\text{-Al}_2\text{O}_3$	54.4–73.6	—	[86]
	TBA	10–25 vol%	AM	MBAM	62.85–76.26	2.46–2.94	[95]
ZrO_2 -mullite	Deionized water	—	—	$\rho\text{-Al}_2\text{O}_3$	47.3–55.6	3.810–5.020	[90]
	Deionized water	—	—	$\rho\text{-Al}_2\text{O}_3$	63.59–70.65	—	[83]
SiO_2 -mullite	TBA	45 wt%	AM	MBAM	71–75	—	[93]
Al_2O_3	TBA	5–15 vol%	AM	MBAM	64–92	0.6–2.2	[87]
	Deionized water	30–40 vol%	AM	MBAM	37.0–47.52	0.2998–0.3719	[92]
Al_2O_3 -YSZ	Deionized water	—	—	$\rho\text{-Al}_2\text{O}_3$	71.1–72.7	—	[84]
SiC	EG	15–35 vol%	AM	MBAM	58.2–74.1	3.08–3.31	[88]
Si_3N_4	Deionized water	25–40 vol%	—	Isobam #104	50–56	—	[96]
	TBA	20–60 wt%	AM	MBAM	42–77	~2	[97]
Y- α -SiAlON	TBA	10–17.5 vol%	AM	MBAM	44.2–58.6	1.87–2.89	[91]
Y_2SiO_5	Deionized water	10–25 vol%	AM	MBAM	73.94–87.70	—	[89]
	TBA	20–50 wt%	AM	MBAM	45–75	~3	[94]
$(\text{Dy}_{0.2}\text{Y}_{0.2}\text{Ho}_{0.2}\text{Er}_{0.2}\text{Yb}_{0.2})_2\text{Zr}_2\text{O}_7$	Deionized water	2.5 wt%	—	Agarose	93.86–97.50	—	[85]

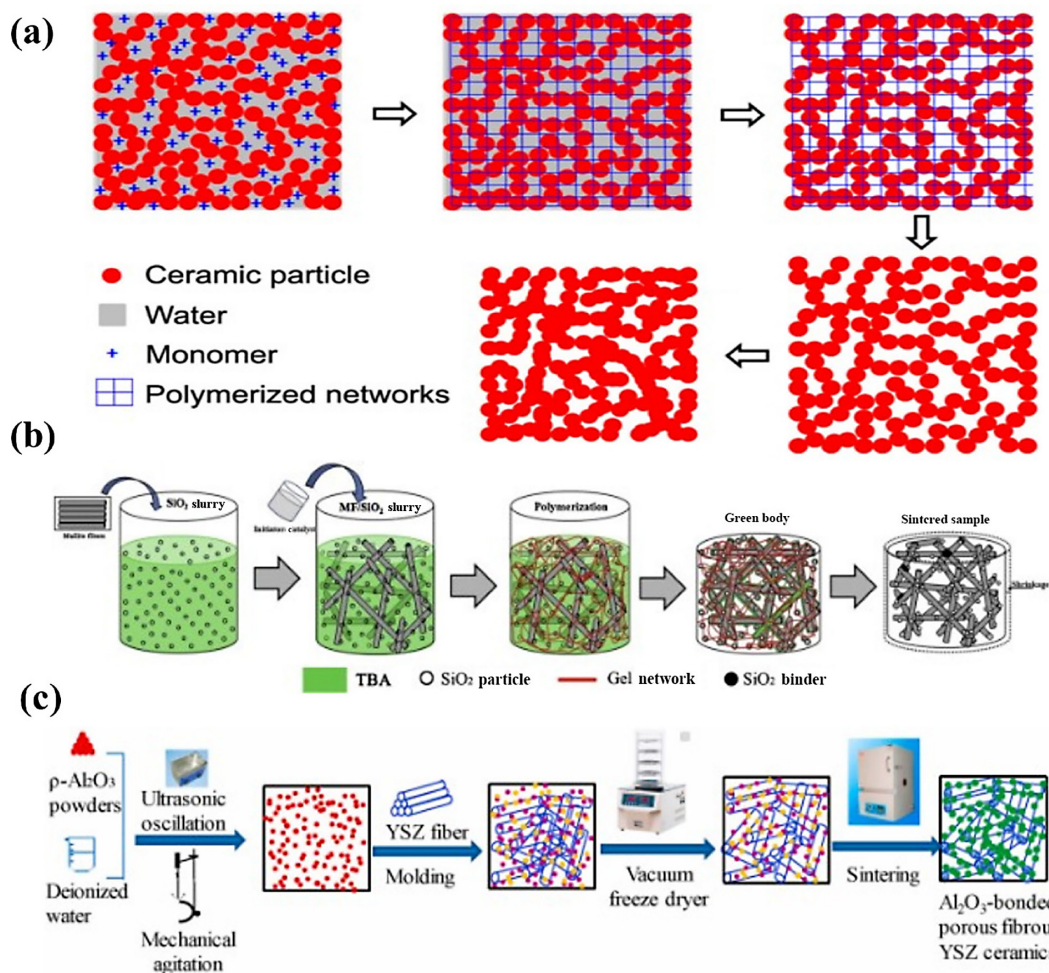


Fig. 4 Schematic diagram of gel-casting system: (a) water based on AM/MBAM. Reproduced with permission from Ref. [92], © The Authors 2018. (b) TBA-based fibrous ceramics. Reproduced with permission from Ref. [93], © Elsevier Ltd. 2012. (c) Water based on $\rho\text{-Al}_2\text{O}_3$ fibrous ceramics. Reproduced with permission from Ref. [84], © Elsevier Ltd and Techna Group S.r.l. 2021.

compressive strengths ranging from 3.45 to 4.24 MPa and thermal conductivities ranging from 0.209 to 0.503 W/(m·K).

The solid loading and gelling contents are important factors of slurry flowability that affect green body formation. Within appropriate limits, increasing the solids content decreases the

porosity and average pore size of the ceramics. Yan *et al.* [95] prepared mullite matrix ceramics via a TBA-based gel-casting process; as the solid loading increased from 10 to 25 vol%, the open porosity decreased from 76.26% to 62.85%, whereas the average pore size increased from 2.46 to 2.94 μm . Using 0.2 wt%

Isobam #104 (a copolymer of isobutylene and maleic anhydride) as dispersants and gelling agents, Wan *et al.* [96] prepared porous Si_3N_4 ceramics, and the porosity varied from 56% to 50% as the solid loading increased from 25 to 40 vol%.

The gel-casting process can produce uniform green bodies with complex shapes and high strength. The low content of organics is conducive to simplifying or even eliminating the particular removal process to leave pores, which is beneficial for preparing ceramics with small pore sizes and narrow pore distributions. However, the porosity is not high enough. This process requires strict drying conditions and solid loading ranges, as improper drying can cause destruction and cracking of the green bodies.

2.5 Foam-gelcasting

Foam-gelcasting combines direct foaming and gel-casting to obtain ceramics with ultrahigh porosity and complex shapes, which utilize foaming agents to generate bubbles with high volume and gelling agents to bind solid particles, greatly enhancing the stability of the foam and the mechanical strength of

the green body. The classical process of foam-gelcasting involves first mixing ceramic particles, foaming agents, chemicals from the gelling system, and solvents, then mechanical stirring to incorporate gas into the previous suspension, followed by initiating the gelling reaction to obtain a green body, drying, binder removal, and sintering to obtain porous ceramics. Table 5 summarizes the features of the porous ceramics fabricated via foam-gelcasting. Figure 6 illustrates the principles of foam-gelcasting and the hierarchical pore structure of the products. Owing to the addition of foaming agents, the porosity increases to approximately 80% and can reach 90% when the solid loading remains below 35 vol% [98–100], and the pore structure clearly changes. Hierarchical pores can be created, while cell pores around hundreds of micrometers are made by mechanical agitation, and smaller pores around tens of micrometers are led by the removal of gelation [101].

The impact factors, including the foaming agent, solid content, and gel system, are the same as those used in the above methods. The type and ratio of surfactants directly influence the properties

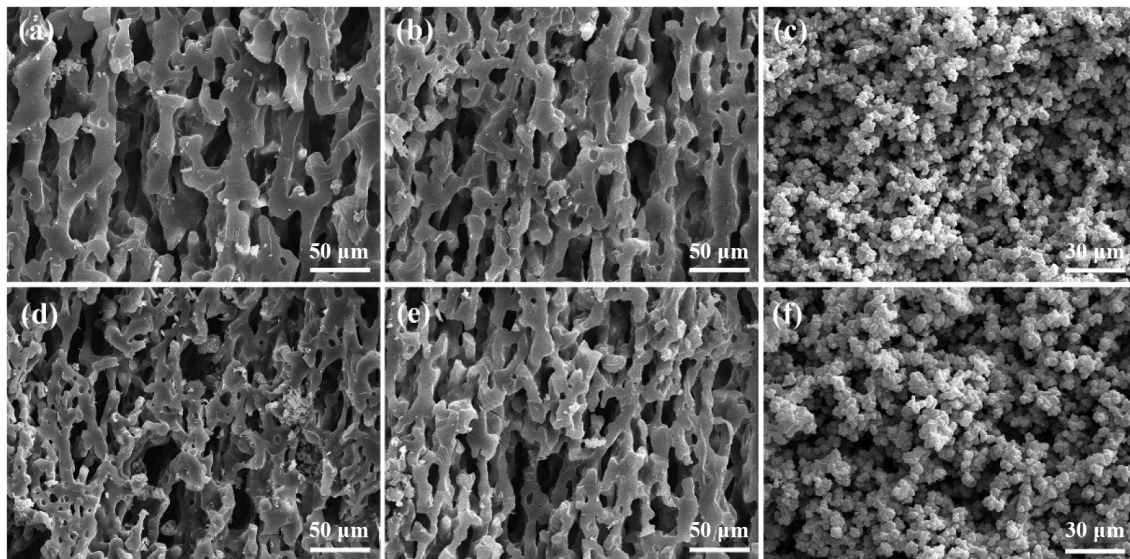


Fig. 5 Microstructures of gels synthesized in (a, d) water, (b, e) EG, and (c, f) TBA. AM/MBAM weight ratio of (a–c) was 30 : 1, whereas that of (d–f) was 5 : 1. Reproduced with permission from Ref. [88], © Elsevier Ltd and Techna Group S.r.l. 2019.

Table 5 Summary of pore features of porous ceramics produced via foam-gelcasting method

Material	Solid loadings	Foam agents	Gelling sources	Porosity (%)	Pore size (μm)	Ref.
MgAl_2O_4	35–40 vol%	SDS	N-methylol acrylamide/MBAM	75.14–82.46	~66.26 (average)	[107]
Al_2O_3	40 vol%	TLS	Isobam 104#	66.4–82.9	124–188 (cell size)	[102]
		DTAC		68.3–82.9	50–89 (cell size)	
	40 vol%	EMAL TD	Isobam 104#	20–89	60–220 (cell size)	[103]
ZrO_2	20–27 vol%	CTAB and sodium N-lauroyl sarcosinate	Isobam 110	45.22–84.04	18.12–146.30 (cell size)	[104]
Mullite	52 vol%	TLS	Isobam 104#	75.3–76.6	252.1–358.8 (average)	[101]
	52 vol%	TLS	Isobam 104#	~67	200–350 (average)	[108]
	40 vol%	DTAC	Isobam 104#	63–67	52–81 (cell size)	[109]
			Isobam 600AF	67–79	29–58 (cell size)	
Mullite– SiO_2	50–65 wt%	SDS	AM/MBAM	25.4–84.1	~64 (average)	[110]
	50 wt%	SDS	AM/MBAM	62.2–86.7	—	[106]
Si_3N_4	20–30 vol%	PG	Isobam 104#	90.8–96.4	100–400	[99]
	22–30 vol%	CTAB and sodium N-lauroyl sarcosinate	Isobam 104#	92–97	100–320	[98]
SiO_2	27–33 vol%	CTAB and sodium N-lauroyl sarcosinate	Isobam 104#	84.61–91.35	—	[100]
SiC-ZrB_2	56.5–64.7 wt%	TLS	Isobam 104#	84.7–87.9	100–200 (cell size)	[111]

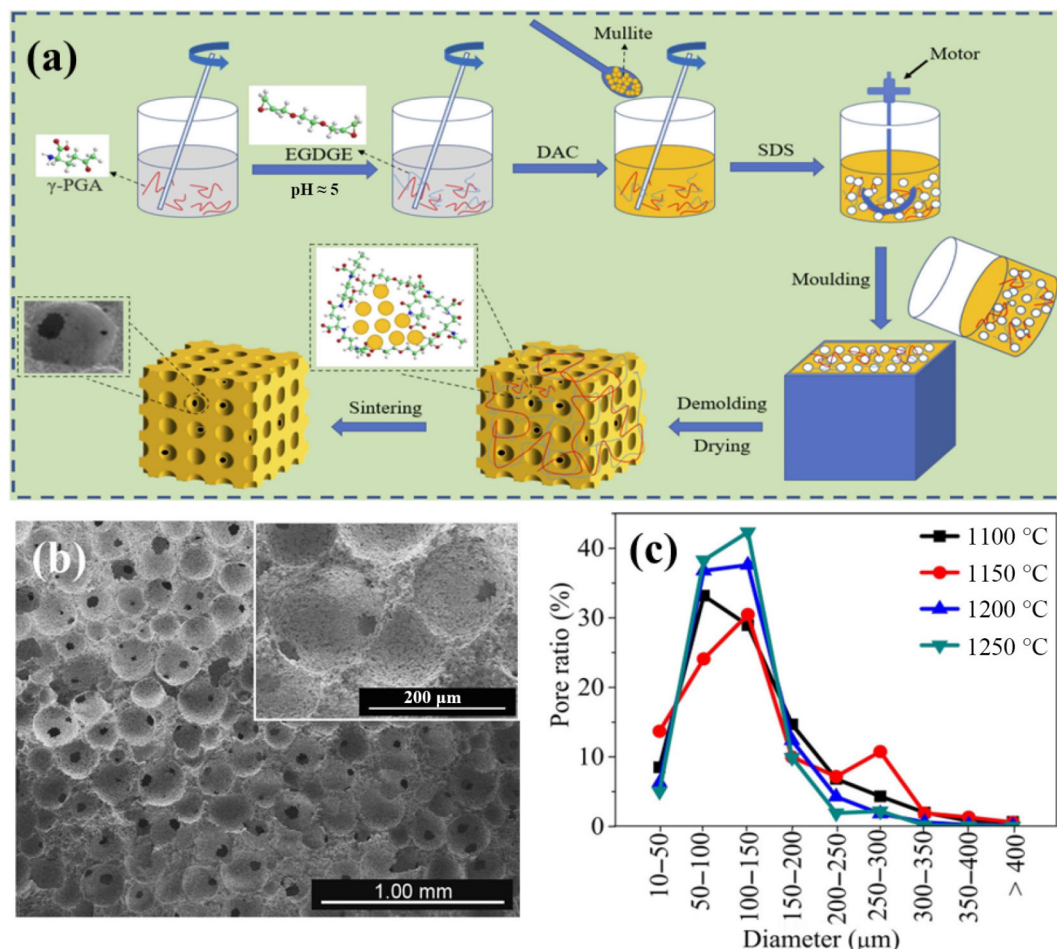


Fig. 6 (a) Schematic illustration of mullite porous ceramics fabricated via foam-gelcasting method. Reproduced with permission from Ref. [105], © Elsevier Ltd. 2022. (b) SEM images of porous ceramics fabricated via foam-gelcasting method. Reproduced with permission from Ref. [106], © Elsevier B.V. 2018. (c) Pore size distribution of porous ceramics fabricated via foam-gelcasting method. Reproduced with permission from Ref. [11], © Elsevier Ltd. 2017.

of porous ceramics. Zhao *et al.* [102] used Isobam 104 as both the dispersant and the gelling agent and cationic DTAC and anionic TLS as different surfactants to prepare Al_2O_3 porous ceramics. The wet alumina foams with cationic DTAC were more stable than those with anionic TLS, which was mainly due to the hydrophobic interaction between anionic PIBM and cationic DTAC but not between PIBM and TLS. Yang *et al.* [103] reported that the porosity and cell size of porous ceramics increased with increasing content of the surfactant $\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{H}\cdot\text{N}(\text{C}_2\text{H}_4\text{OH})_3$ (EMAL TD). The porosity and pore size are affected by the stabilization of foams, while the slurry viscosity also influences the pore structure. The foam volume expansion ratio decreased with increasing slurry viscosity, resulting in lower porosity. Leng *et al.* [104] prepared porous zirconia ceramics, the porosity of which decreased from 84.04% to 45.22% with increasing slurry viscosity through changes in the ratio of surfactants.

The pore diameter produced by direct foaming typically falls within the range of several hundred micrometers. With the addition of a gel system, ceramic particles are bonded and thickened the foam walls, whereas, during the removal of the gel, small pores of approximately several tens of micrometers are formed on the walls of larger pores. As a result, porous ceramics prepared by foam-gelcasting usually exhibit a hierarchical pore structure. Han *et al.* [101] prepared porous mullite ceramics with porosities ranging from 75.3% to 76.6% and pore sizes ranging from 1 to 800 μ m using TLS as a foam agent and Isobam 104 as a gelling agent. Among all the pores, the large pores at

approximately 300 μ m were due to the air produced by the foaming process, the smaller pores at approximately 20 μ m were formed by the elimination of organics, and the smallest pores at approximately 1 μ m occurred due to the accumulation of ceramic particles; consequently, the porosity was increased by the presence of small interconnected pores. With increasing sintering temperature, all the pore sizes clearly decreased.

The method overcomes the drawbacks of the two forming methods, which do not require strict drying conditions, making it easier to demold and shape the green body. With the participation of the gelling agent, the foam exhibits increased stability and uniformity, producing porous ceramics with high strength and a hierarchical pore structure.

2.6 Additive manufacturing

In contrast to traditional subtractive manufacturing methods, additive manufacturing, also referred to as 3D printing, is a layer-by-layer manufacturing method conforming to the three-dimensional model in CAD software, which can be divided into extrusion and jetting-based techniques (e.g., direct ink writing (DIW), inkjet printing), photopolymerization-based techniques (e.g., stereolithography, digital light processing (DLP), two-photon polymerization), and powder sintering/melting-based techniques (e.g., selective laser sintering (SLS)/melting) according to the processing of the starting materials [42,112,113]. AM has become a preferred approach to fabricating components with complex geometry and high precision, which could achieve material

savings and personal customization. In addition to the porous struts built by AM with the assistance of the hollow microsphere method [114], bubble or emulsion droplet templates [115], and freeze-casting [116], the porous structure constructed only by AM is derived from the 3D model and is present in the form of a periodic framework. Therefore, the porous structure directly derived from AM is limited by the forming accuracy, and the pore size distribution ranges from hundreds of micrometers to several millimeters for the direct ink writing technique to 1–2 μm for the two-photon polymerization technique [41]. Next, three kinds of typical AM techniques are discussed: DIW, DLP, and SLS.

DIW relies on the extrusion of slurries with suitable rheological properties involving high viscosity, shear thinning behavior, and sufficient yield stress and can be used to prepare products with simple periodic lattice structures, the printing accuracy of which is relatively low above 100 μm [117,118]. Owing to the porous structure derived from the framework constructed by the extruded filaments, the rheological performance and density of the feedstock, the nozzle diameter and shape, the printing path, and the drying and sintering strategies are crucial factors for the porous structure. On the basis of the Herschel–Bulkey equation, a minimal value of the shear-thinning exponent and viscosity parameter are favorable for extrusion and mixing, whereas a high yield stress is necessary for shape retention after extrusion [118].

Zocca *et al.* [119] proposed that a sufficient storage modulus of 10^5 – 10^6 Pa and yield stress of 10^2 – 10^3 Pa are required for the ink, whereas Minas *et al.* [115] reported that inks with storage moduli above 2 kPa and yield stresses above 200 Pa are printable. Chan *et al.* [120] proposed an improved criterion for predicting the printability of ink on the basis of the yield stress (τ_y), storage modulus (G'), and recovery of the storage modulus ($G'_{\text{recovered}}$), as indicated in Eqs. (2) and (3), where the constant C_1 is refined to approximately 5×10^6 , whereas the constant C_2 is approximately 6×10^{10} (Fig. 7). As shown in Fig. 8, Tang *et al.* [31] utilized DIW to directly prepare nanosized MgO-strengthened alumina-based ceramics with porosities of 35%–48%, and the filament-surrounded pore size was approximately hundreds of micrometers.

$$G' = \frac{C_1}{\tau_y} \quad (2)$$

$$G'_{\text{recovered}} = \frac{C_2}{G' \times \tau_y} \quad (3)$$

To further improve the porosity and broaden the application scope, various methods for secondary pores on the struts have been combined with DIW, such as the hollow microsphere

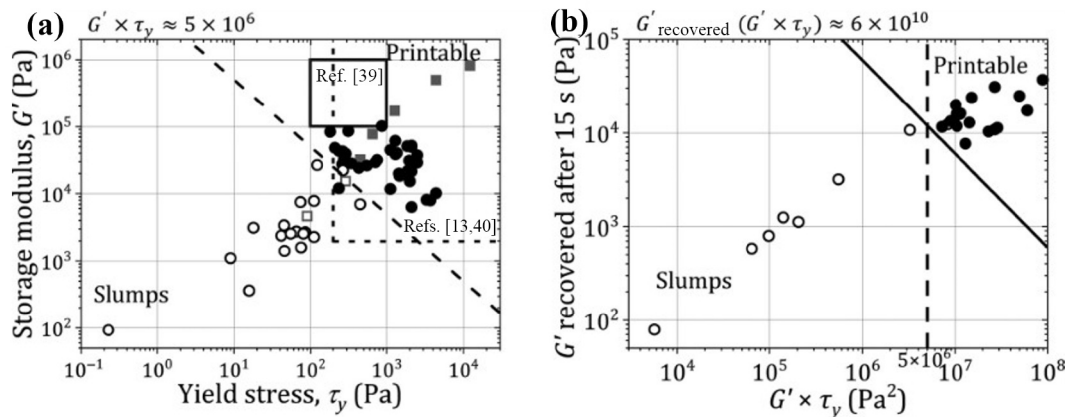


Fig. 7 (a) Printability plot of storage modulus against yield stress; (b) $G'_{\text{recovered}}$ after 15 s from the end of a high shear stress interval plotted against the product of G' and τ_y . The diagonal lines indicate a possible printability boundary separating printable from unprintable inks. Reproduced with permission from Ref. [120], © The American Ceramic Society 2020.

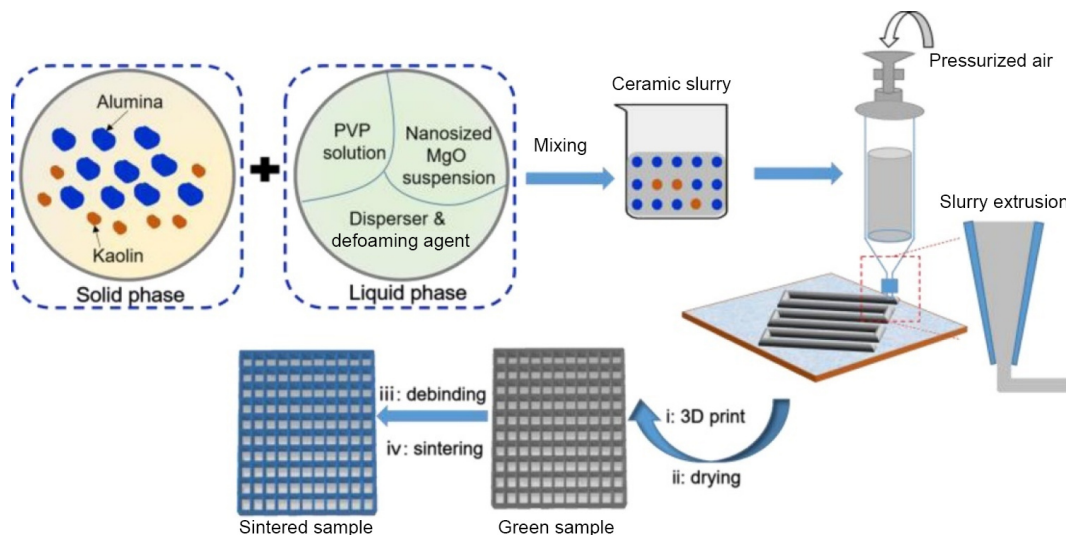


Fig. 8 Schematic diagram of DIW process. Reproduced with permission from Ref. [31], © Elsevier Ltd. 2020.

method, particle-stabilized foams or emulsions, freeze drying, and partial sintering methods, and the critical premise is the rheological property regulation of suspensions [115,121–123]. Huo *et al.* [121] designed aqueous suspensions composed of hollow microspheres, bentonite nanoparticles, and hydroxypropyl cellulose as feedstock for DIW, the storage modulus and yield stress of which could be increased to 830 kPa and 1491 Pa due to the percolating network of bentonite nanoparticles, resulting in pores smaller than 100 μm generated from the hollow microspheres and their interstices and low sintering shrinkage of 7.0%–8.0%, benefiting from the dense shells of hollow ash microspheres (Fig. 9). Minas *et al.* [115] proposed the fabrication of hierarchical porous ceramics by combining DIW and emulsion/foam templating, and the storage moduli and yield stress of emulsions were adjusted to be suitable (storage moduli of 134.7 and 28.7 kPa, yield stresses of 1183 and 491 Pa) for DIW by increasing the propionic acid concentration to 0.08 mmol/g and adding 0.5 or 2 wt% PVA, contributing to the porous filaments with a mean pore size of 4.6–17.4 μm .

As a typical photopolymerization-based technique, DLP has a higher resolution of approximately 1 μm and a printing speed of approximately 30 mm^3/s , allowing the fabrication of components with complex geometries, fine structures, and smooth surfaces [124]. By exposing a homogeneous suspension composed of ceramic particles and photosensitive resin to ultraviolet light, instantaneous entire-layer polymerization can be stimulated via digital micromirror devices, and layer-by-layer solidification can lead to the creation of porous materials with designed structures [41,125]. Thus, the designed geometries, types, and contents of chemicals used for polymerization, printing, and heat treatment parameters affect the porous structure of the final products. The rheological behavior and stability of ceramic suspensions should be well controlled to meet the requirements of the DLP process

and the structural integrity and uniformity, which are directly determined by the particle size distribution, solid loading, monomers, diluents, and dispersants. Generally, an ideal ceramic suspension for DLP should possess a decreased viscosity immediately after recoating, instantaneous recovery after recoating, and good stability to inhibit concentration gradients during DLP printing [126]. Zhang *et al.* [127,128] prepared Pickering emulsions with various oil-to-water ratios as feedstocks for DLP, where suitable rheological performance with shear-thinning behavior and elastic solids at low shear stress, as well as excellent stability free from phase separation and emulsion droplet changes, was found for the DLP process (Fig. 10).

In addition, ceramic particles with high refractive indices and light absorption involving Si_3N_4 and SiC , present great challenges for preparing complex shape parts via DLP, which has been solved by surface modification and emerging PDCs [129–131]. To realize DLP for SiC particles, preoxidation treatment of SiC was conducted by Han *et al.* [129], and a suspension with a high solid content of 55 vol% and viscosity of 7.77 Pa·s was prepared, contributing to an enhanced curing thickness of more than 50 μm . However, the synthesis of photosensitive organosilicon polymers, ceramic yield, and increased sintering shrinkage (usually greater than 25%) are the main concerns for PDC. He *et al.* [131] introduced a considerable amount of SiO_2 powders as a filler into low-solid-weight polysiloxane to increase the ceramic content and reduce the degree of thermal shrinkage to within 10%, as illustrated in Fig. 11(b).

During SLS, there is no need for the preparation of slurries, but high-energy lasers to locally heat ceramic powders above the melting point are needed and then cooled to form dense interlayer structures. Unlike selective laser melting (SLM), which uses ultrahigh power to melt powders, the laser power in SLS is just sufficient to fuse particles (Fig. 12), but ceramics with high melting

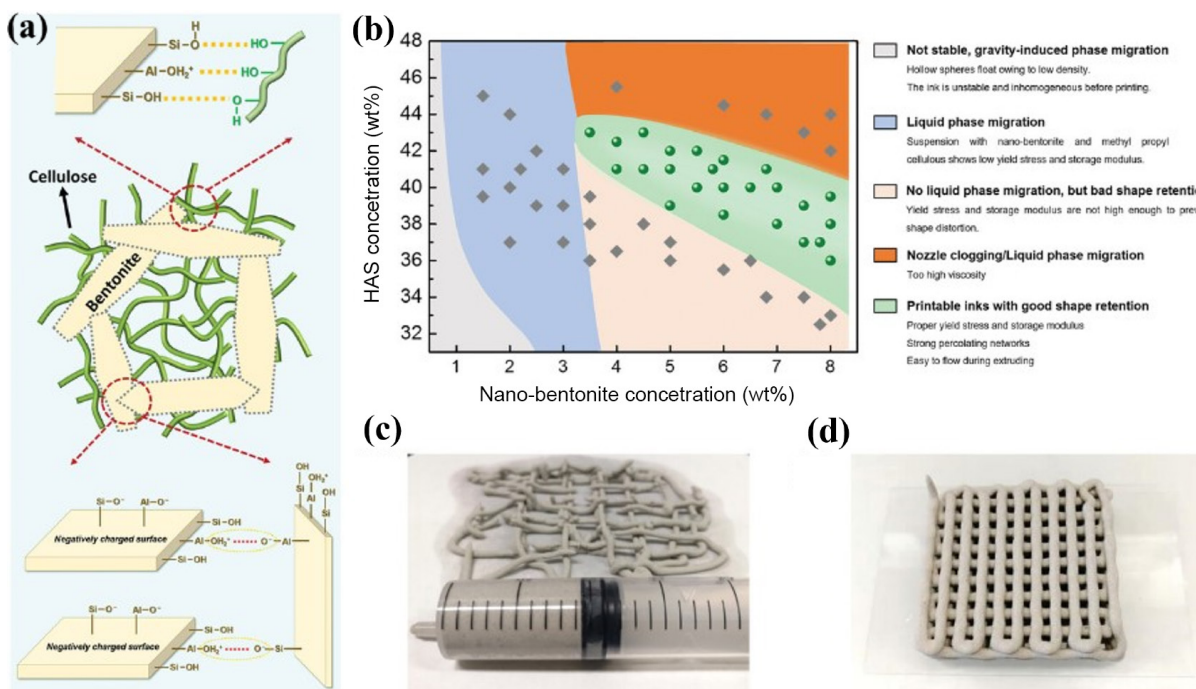


Fig. 9 Expected microstructure and printability of suspensions containing hollow spheres, bentonite nanoparticles, and hydroxypropyl cellulose. (a) Schematics illustrating molecular interactions expected to occur within percolating network of bentonite nanoparticles and between bentonite surfaces and hydroxypropyl cellulose molecules. (b) Diagram displaying concentrations of bentonite nanoparticles and hyaluronic acid (HA) microspheres required to obtain printable inks with good shape retention (green area) and the printability issues encountered outside optimum ranges. (c) Representative ink that undergoes liquid phase migration during printing. Liquid migration leads to a lower water content in ink inside syringe than in the printed filaments. (d) Example of a grid-type structure manufactured using a homogenous printable ink (green area in (b)). Reproduced with permission from Ref. [121], © The Authors 2023.

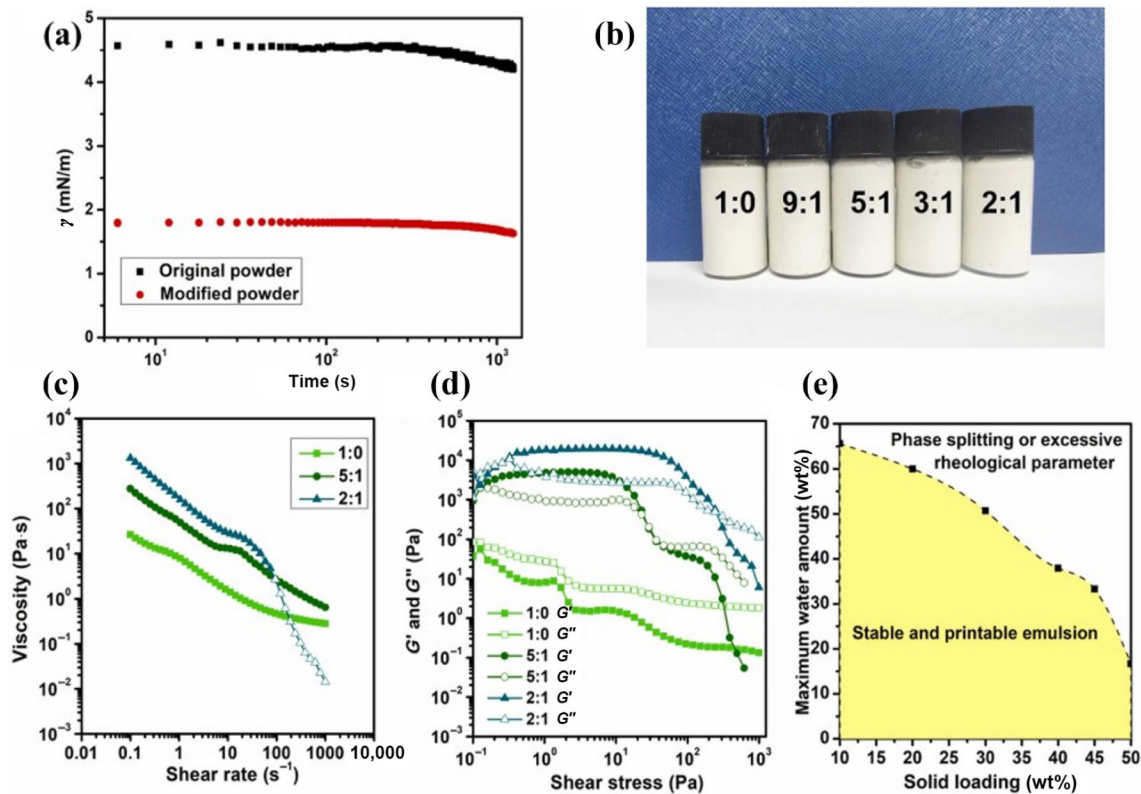


Fig. 10 (a) Dynamic interfacial tension of suspensions composed of water, HDDA, and mixed particles before and after modifier addition. (b) Photographs of oil-based suspension and Pickering emulsions with different oil-to-water ratios after standing for two weeks. (c, d) Rheological properties of oil-based suspension and Pickering emulsions with different oil-to-water ratios: (c) viscosity as a function of shear rate and (d) modulus variation with shear stress. (e) Diagram displaying water amount and solid loading to obtain pastes with printable rheological properties and stability. Reproduced with permission from Ref. [127], © Elsevier B.V. 2023.

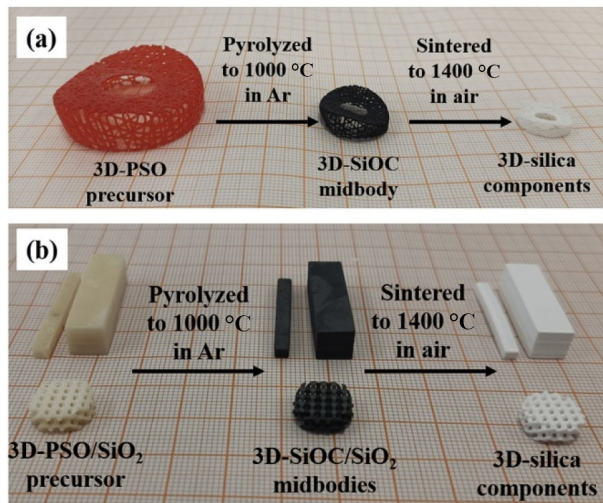


Fig. 11 Influence of SiO_2 fillers on sintering of polysiloxane. (a) TSAA sintering process of 3D-PSO precursor and (b) TSAA sintering process of 3D-PSO/ SiO_2 precursor with the addition of SiO_2 powders. Each small bar in this graph was 1 mm. Reproduced with permission from Ref. [131], © Elsevier Ltd. 2021.

points still challenge the applications of SLS, and the common issues include low precision, high porosity, and heterogeneity, and poor mechanical properties [41,132]. Therefore, ceramic powders should first be granulated to the micron scale from nano- or submicron scales or coated with a binder (e.g., $\text{NH}_4\text{H}_2\text{PO}_4$, epoxy resin, or Al) when utilized for SLS. Despite the designed porous structure, the morphology, particle size distribution, and sintering behavior of ceramic powders, printing, and posttreatment parameters influence the pore structure of the skeleton. Currently,

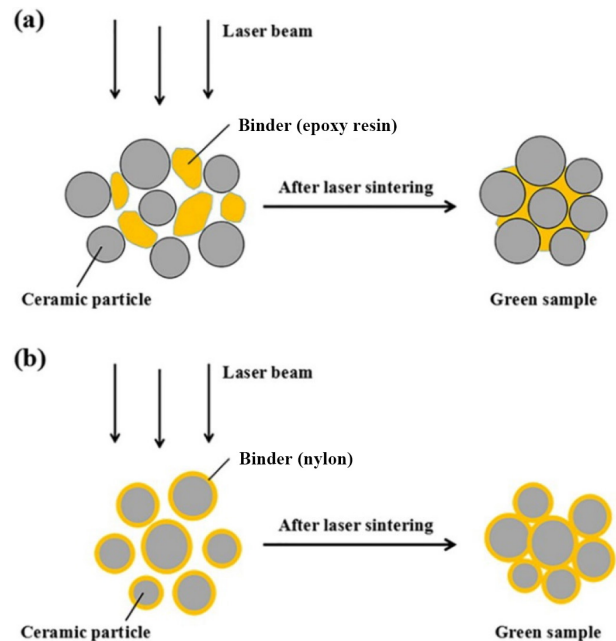


Fig. 12 Schematic diagrams of SLS mechanism for preparing ceramic green samples using ceramic powders (a) mixed and (b) coated with binders. Reproduced with permission from Ref. [137], © Institute of Materials, Minerals and Mining 2017.

porous ceramics with various systems, including Al_2O_3 [133], mullite [134], Si_3N_4 [135], and SiC [136], have been prepared via SLS. By adding AlN as the inorganic binder, porous Si_3N_4 ceramics with an enhanced flexural strength of 23.9 MPa at a

porosity of 33.6% were prepared by Wu *et al.* [135], which could be due to the fracturing route across the poly-hollow microspheres. Chen *et al.* [134] prepared mullite pores with porosities ranging from 57.7% to 67.7% and bimodal pore structures via SLS and reported that uncompacted powder layers and the removal of sacrificial binders increased the total porosity of ceramics.

Although constrained by forming precision, AM enables the fabrication of porous ceramics with a wide range of porosities, variable macropores, and complex structures. It leverages CAD technology during the design phase for the adjustment and optimization of both the shape and internal architecture of components. The construction of intricate internal structures is facilitated through the layer-by-layer deposition of materials. The monolithic fabrication enables the direct printing of complex structures, eliminating the need for assembly and postprocessing steps. Moreover, it can be combined with techniques such as direct foaming and pore-forming agent methods to adjust pore structures, thereby offering new possibilities for the preparation of biomimetic porous materials, especially for given scenarios.

2.7 Other processes

In addition to the aforementioned preparation methods, freeze-casting [138], phase inversion [139], and template replication [140] are also commonly used to fabricate porous ceramics with specific pore structures.

Freeze-casting involves freezing a liquid colloidal suspension, followed by sublimation of the frozen phase to achieve the desired pore structure. When unidirectional or gradient freezing is applied, it can be used to produce porous ceramics with directional interconnected pores [141]. Huang *et al.* [142] fabricated a porous SiC ceramic membrane with a unidirectional gradient pore microstructure via a unidirectional freeze-casting process (Fig. 13(a)). In this method, the porosity and pore structure are influenced by the solid content of the slurry as well as the direction and temperature gradient during freeze-drying.

Phase inversion, which involves dissolving a polymer in a suitable solvent and shaping it into a desired form (such as a thin film, tube, or hollow fiber), was developed for the preparation of polymer membranes. The addition of a precipitant or nonsolvent induces phase separation, resulting in a solid polymer phase and a liquid solvent phase. The precipitated polymer then forms a porous structure characterized by a network of relatively uniform pores [143]. This method has been explored for the preparation of porous ceramic membranes, especially those with hollow fiber geometry [139,144]. Figure 13(b) shows the principles of the phase inversion method and the typical pore structure. Porous ceramic membranes with low porosity (below 40%) for separation and filtration can be obtained via phase inversion combined with tape casting [145,146].

The template replication method uses a porous organic foam with open pores as a template. The ceramic slurry is infiltrated into this template, which is then subjected to heat treatment. During the heating process, organic materials are burned out, leaving a ceramic body with pore structures that replicate the template [147]. Faure *et al.* [148] obtained porous Al_2O_3 ceramics via the impregnation of polyester-based polyurethane (PU) foams (Fig. 13(c)). The resulting ceramic framework is dense, with the pore structure and dimensions precisely mirroring those of the template. Thus, the main advantage of this method is easy control of the porosity and pore structure through the selection of an appropriate template [149].

Moreover, several new methods have been introduced to

prepare porous ceramics with special structures. $\text{La}_2\text{Zr}_2\text{O}_7$ ceramics with a “Voronoi foam” structure were fabricated on the basis of *in situ* pore formation [150]. The pore-forming agent nanosized carbon spheres were covered by ceramic powders to form a precursor with a shell–core structure instead of dispersing in the particles or the slurry. Thus, hollow-grained ceramics were obtained with the removal of carbon spheres during the sintering process. Directional solidification is commonly used to prepare dense metallic materials, whereas Zhao *et al.* [151] creatively fabricated porous ceramics via this method. The three-phased porous ceramics (Al_2O_3 – $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG)– ZrO_2) obtained by the *in situ* generation of lotus-type directional pores exhibited an ultrahigh flexural strength of 497 MPa with a porosity of 34% at ambient temperature. The combination and innovation of preparation methods can enhance the development of porous ceramics with larger sizes and better properties, which is of positive significance for industrial applications.

3 Principles of low sintering shrinkage

The sintering linear shrinkage is determined by the equation: $\text{Shrinkage} = [(l_a - l_b)/l_a] \times 100\%$, where l_a and l_b are the lengths of the green bodies and sintered samples, respectively. Typically, the sintering shrinkage rate of ceramics is above 10% [152]. Ceramics with a sintering shrinkage rate below 10% are defined as low sintering shrinkage ceramics in this review (unless specified, shrinkage refers to linear sintering shrinkage). Porous ceramic sintering can be defined as the process of atomic diffusion and bicontinuous microstructure formation between particles with the application of heat. Moreover, at the macroscopic scale, the process is accompanied by strengthening and shrinkage. From a mechanistic point of view, sintering proceeds via surface diffusion, volume diffusion, grain boundary diffusion, evaporation–condensation, plastic deformation, or creep (if pressure is applied). Surface diffusion and evaporation–condensation alone cannot lead to shrinkage or densification directly [43]. Typically, the common methods used to prepare porous ceramics with low sintering shrinkage include (i) the generation of volume expansion phases by reactions and phase-transition sintering [121,153,154]; (ii) the construction of rigid skeletons by fibers, whiskers, particles, and strongly bonded phases [93,155,156]; (iii) the impact on specific mass transfer processes such as surface diffusion [157]. On the basis of various principles, several low sintering shrinkage porous ceramics have been prepared, such as mullite-based [29,158], Al_2O_3 -based [133], and $\text{SiC}/\text{Si}_3\text{N}_4$ -based [157,159] ceramics. In addition to the factors of the sintering process, such as temperature and solid loading, three main principles for achieving low sintering shrinkage are introduced (Fig. 14):

- 1) Generate the expansion phases to reduce shrinkage.
- 2) Construct rigid skeletons to resist shrinking.
- 3) Select material systems to regulate the specific mass transfer process.

3.1 Generation of expansion phases

The sintering shrinkage can be offset by the expansion phases. Common reactions capable of generating expansion phases include reaction sintering, phase transition reactions, and oxidation reactions.

The mullitization reaction is a typical form of reaction sintering, in which the formation of expansion phase mullite from different raw materials can reduce shrinkage. Lü *et al.* [163] explored the sintering behavior of mullite via dilatometry with the recycling of coal gangue and bauxite as raw materials. Above 800 °C, the initial trend increased, followed by a decrease, where

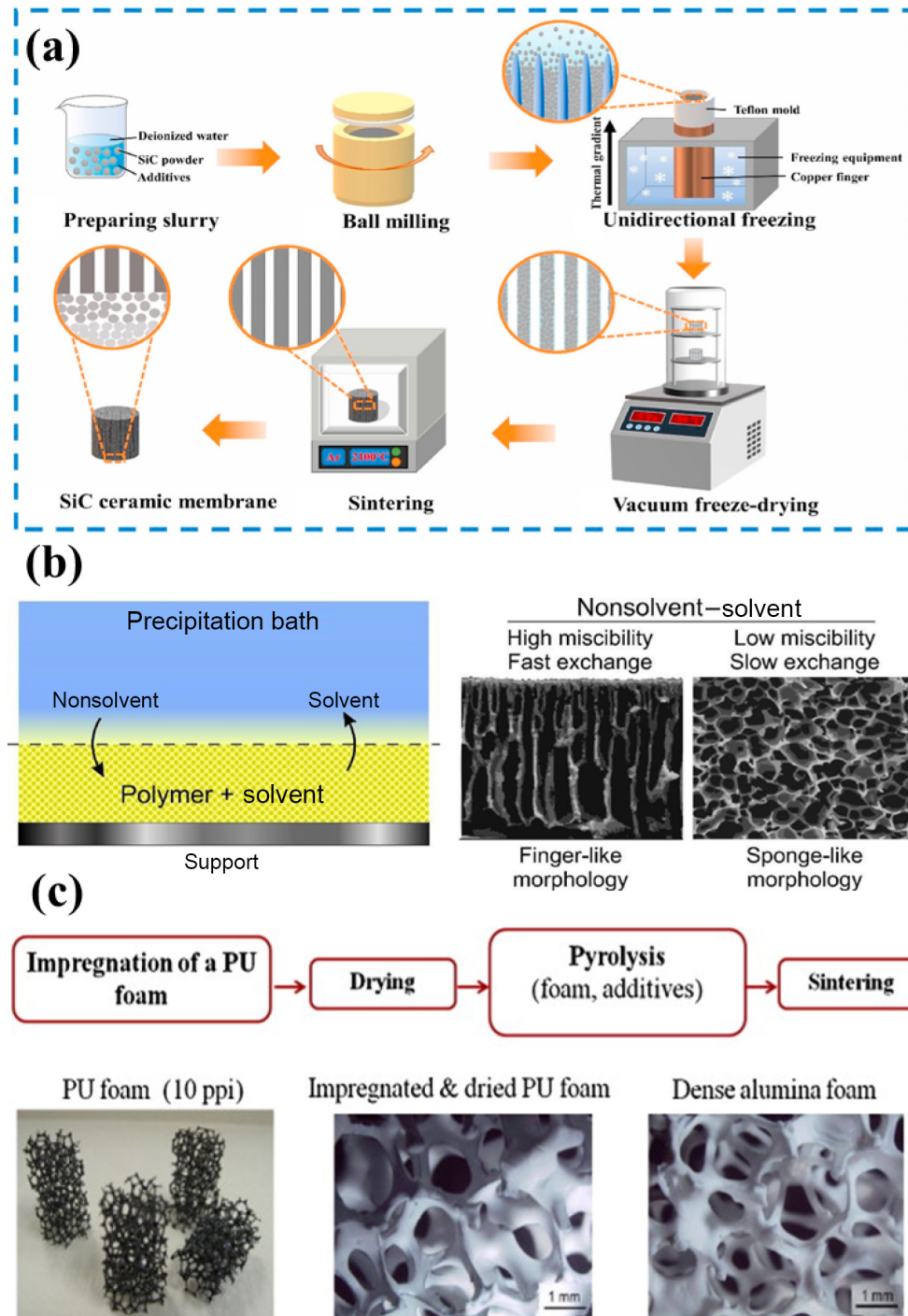


Fig. 13 Schematic diagrams of (a) freeze-casting. Reproduced with permission from Ref. [142], © Elsevier Ltd. and Techna Group S.r.l. 2021. (b) Phase inversion. Reproduced with permission from Ref. [39], © Elsevier Ltd. 2017. (c) Template replication. Reproduced with permission from Ref. [148], © Elsevier Ltd. 2010.

there was a maximum shrinkage of 2.25% at 1276 °C. During the volume-expansion process (1.06%) from 1276 to 1481 °C, secondary mullitization occurred, followed by anisotropic growth of mullite crystals, resulting in volume expansion with increasing temperature, and gradual densification was not normally observed. Lü *et al.* [163] prepared porous mullite ceramic supports via corn starch as a pore-forming agent at 1350 °C. The open porosity increased from 39.67% to 48.12%, and the shrinkage increased from 2% to 7% with increasing corn starch content, as more pores were created and diminished, resulting in a decreased sample volume. Using mullite precursor powders as raw materials, Choo *et al.* [164] obtained porous mullite ceramics with a porosity of 46% and shrinkage of 1.7%.

The high-temperature sintering of kyanite is a phase transition reaction involving structural rearrangement and atomic position changes, resulting in the formation of mullite (an expansion phase). With kyanite and α - Al_2O_3 powders as raw materials, Yan *et al.* [95] produced porous mullite matrix ceramics via gel-casting and pressureless sintering, and the samples sintered at 1500 °C presented 57.15% porosity and 7.93% shrinkage. Guo *et al.* [165] fabricated porous mullite ceramics using kyanite with $\text{Al}(\text{OH})_3$ as a pore-forming agent, which exhibited high apparent porosity (35%–61%) and low shrinkage (–2%–10%).

Aluminum powders are commonly used raw materials for preparing low sintering shrinkage ceramics, and the high-temperature oxidation process of aluminum powders can induce

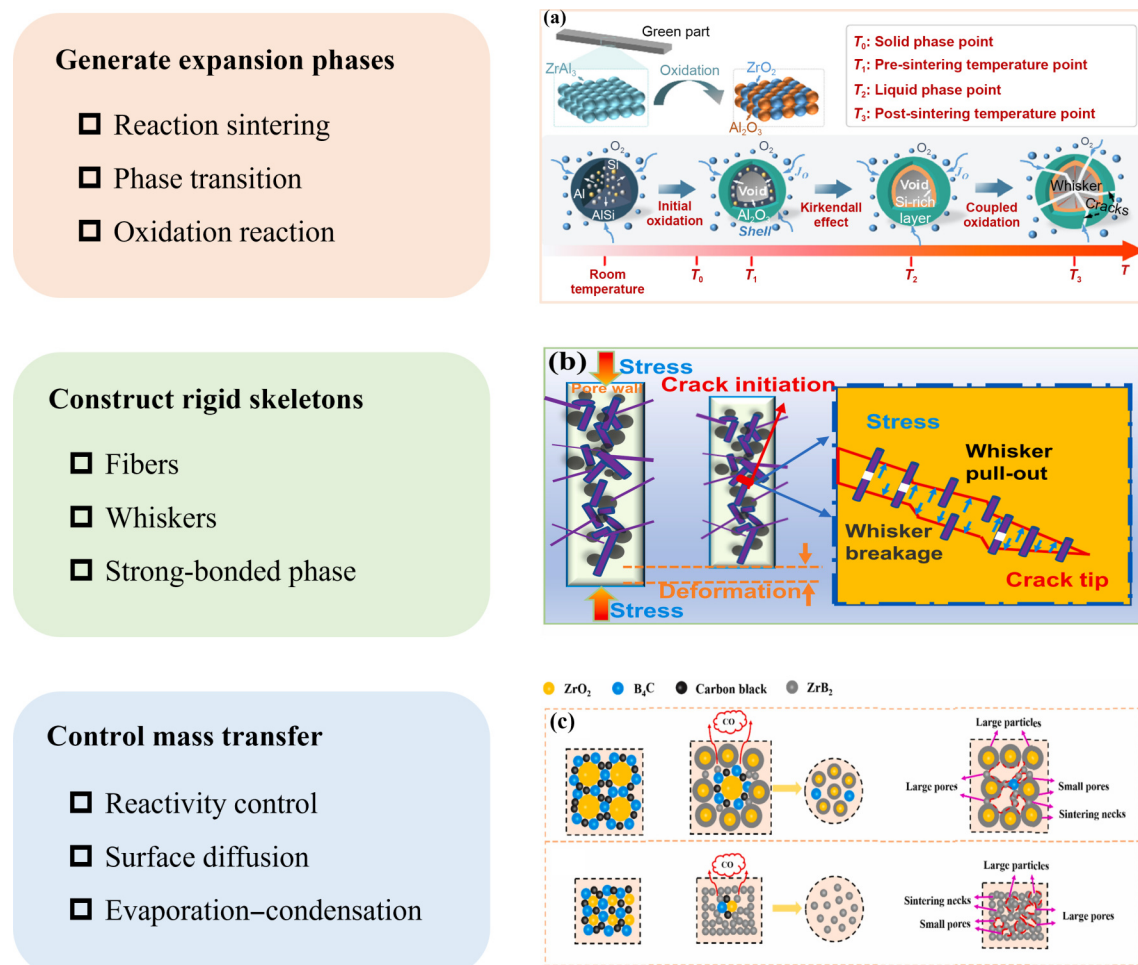


Fig. 14 Schematic diagrams of (a) expansion mechanisms of ZrAl_3 and $\text{Al}_{75}\text{Si}_{25}$ in sintering process. Reproduced with permission from Ref. [160], © Elsevier Ltd. 2023. (b) Enhancement mechanisms of whiskers. Reproduced with permission from Ref. [161], © Elsevier Ltd. and Techna Group S.r.l. 2022. (c) Preparation of ZrB_2 porous ceramics using large and small ZrO_2 particles. Reproduced with permission from Ref. [162], © Elsevier Ltd. and Techna Group S.r.l. 2022.

the Kirkendall effect, leading to significant volume expansion and the formation of hollow spherical aluminum oxide. Xia *et al.* [154] produced open-cell Al_2O_3 ceramic foams using Al powders via foam-gelcasting and freeze-drying. The foams were assembled from hollow Al_2O_3 particles resulting from the Kirkendall effect, as depicted in Fig. 15. The samples had porosities of 89.45%–92.33% and shrinkages of –4.72%–5.88%. The nitridation of silicon powders is similar, which can result in volume expansion through the generation of Si_3N_4 . By using freeze-casting with silicon powders as the initial materials, Hu *et al.* [141] obtained porous Si_3N_4 ceramics with a high porosity of 70.51% and ultralow shrinkage of 0.90%.

In conclusion, the volume expansion due to mullitization, phase transition, and oxidation reactions can all be attributed to the generation of new phases, accompanied by weight gain. Thus, mullite, Al_2O_3 , and Si_3N_4 are commonly chosen as the target products of low sintering shrinkage porous ceramics. The core to restrict shrinkage is to regulate the composition of the raw materials to control the extent of expansion.

3.2 Construction of rigid skeletons

Shrinkage relies on particle rearrangement and grain boundary migration, whereas rigid frameworks typically consist of whiskers, fibers, or strongly bonded phases, which are unfavorable for particle rearrangement or atomic migration.

Whiskers generated by *in situ* reaction sintering not only

increase the porosity of porous ceramics but also resist sintering shrinkage. MoO_3 improves *in situ* mullite whisker growth mainly by reducing the melting point of amorphous SiO_2 and changing the crystal structure of Al_2O_3 . Liu *et al.* [166] prepared porous mullite whisker ceramics using coal gangue powders, $\text{Al}(\text{OH})_3$ and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (as a source of MoO_3) sintered at 1400 °C, with a porosity of 47.2% and a shrinkage of 5%. Huo *et al.* [167] investigated the effect of MoO_3 on the performance of porous mullite ceramics and reported that as the amount of MoO_3 increased from 0 to 15 wt%, the porosity increased from 48.0% to 49.9%, whereas the shrinkage decreased from 0.49% to –0.63%. Owing to the microstructure changing with various MoO_3 amounts (Fig. 16(a)), the generation of needle-like mullite whiskers with high aspect ratios results in network structures that resist shrinkage.

The framework structure composed of fiber materials and binders is stable because the binder firmly adheres to the interlocking fibers, forming numerous strong nodes and thereby reducing sintering shrinkage. Using mullite fibers as the raw materials and silicon resin as the binder, Dong *et al.* [168] fabricated mullite fibrous ceramics with high porosity (81.6%–82.3%) and low shrinkage (1.8%–2.8%) via the molding method. Figure 16(b) shows SEM images of the fibrous ceramics sintered at 1500 °C. The 3D mullite fibrous skeleton structure bonded with silicon provided a relatively stable frame during the sintering process to resist shrinkage. Zhou *et al.* [169] prepared

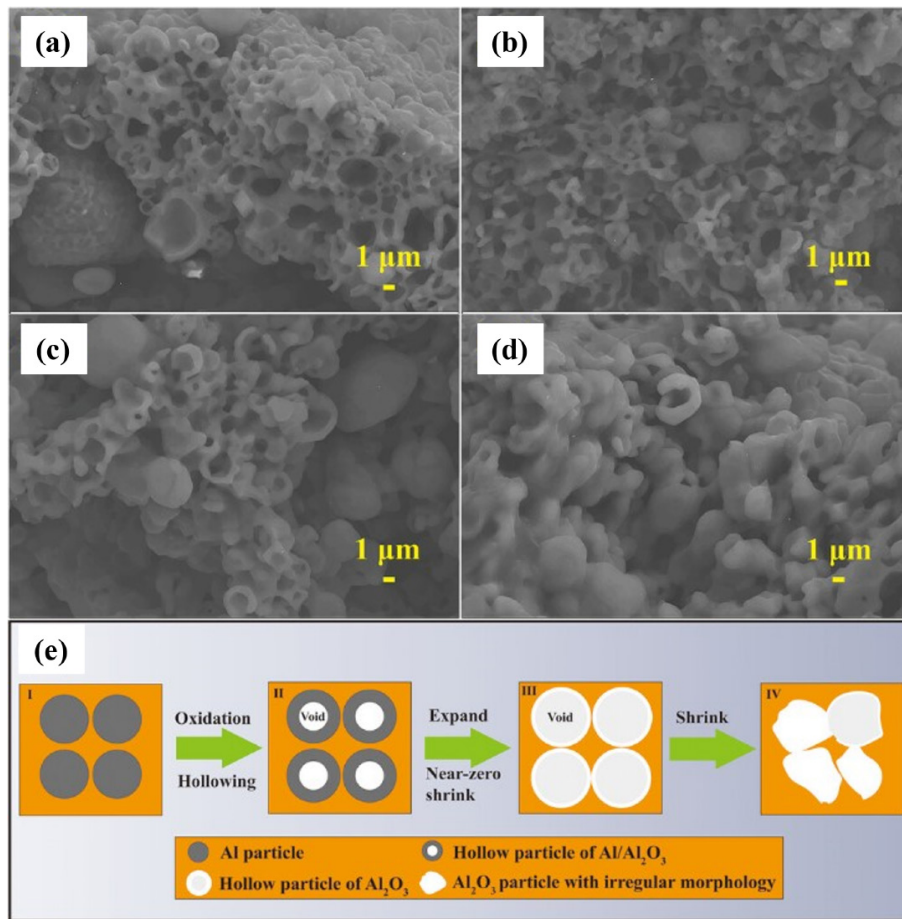


Fig. 15 Morphology of alumina particles at different sintering temperatures: (a–d) 50 wt% solid loading, 1573–1873 K; (e) schematic illustration of shrinkage in alumina foams from Al particles. Reproduced with permission from Ref. [154], © The American Ceramic Society 2023.

fibrous porous silica ceramics via the use of chopped silica fibers as the matrix, boron nitride, and potato starch as binders. The porosity ranged from 91.5% to 94.5%, and the radius shrinkage ranged from –3.61% to 5.33%, especially for the sample sintered at 1050 °C which achieved zero shrinkage.

The difficulty of shrinkage in porous structures composed of strongly bonded phases lies in the strong interparticle bonding, which hinders particle rearrangement. Yang *et al.* [170] proposed a method to fabricate low-shrinkage porous Si₃N₄ by the addition of a small amount of carbon. The addition of carbon promoted the formation of SiC and decreased SiO₂. Moreover, Si₃N₄ was bonded together by the SiC particles (Fig. 16(c)). The densification of Si₃N₄ through particle rearrangement was inhibited by the surface SiC particles formed during the reaction, which strongly pin the grain boundaries. A decrease in SiO₂ inhibited the formation of the glass phase. These two reasons resulted in net-shaped sintering, and the samples sintered at 1750–1850 °C presented porosities ranging from 49.2% to 58.3% and shrinkages ranging from 1.26% to 3.54%.

This principle does not involve phase changes but focuses on microstructures composed of particles or fibers. The rigid frameworks can be formed by particles with tight bonding or strong sintering necks and fibers with firm inorganic nodes. Specifically, fibrous porous ceramics are potential materials for use as low sintering shrinkage ceramics.

3.3 Regulation of the specific mass transfer process

In solid-phase sintering, the process involves only bonding

between solid-phase particles, and mass transport during sintering primarily occurs through mechanisms such as diffusion, interface migration, and surface diffusion. During the sintering process, the temperature, solid content, and sintering additive affect mass transfer. A low temperature, high solid content, and insufficient glass phase (usually caused by the melting of certain components or the addition of additives) reduce particle rearrangement, thereby lowering the shrinkage rate. Moreover, specific mass transfer processes (surface diffusion and evaporation–condensation) lead to only grain coarsening without extensive particle rearrangement.

Low-reactivity initial materials imply slow reaction rates between the chemical constituents, whereas the bonding between particles also proceeds relatively slowly. Therefore, low-reactivity initial raw materials can be utilized to mitigate the shrinkage of the final product without the formation of an expansion phase. Conversely, for the reactions that generate the expansion phase, highly reactive starting materials are indispensable for promoting mass transfer. López *et al.* [171] prepared porous mullite from alumina, a MoO₃ precursor, and two kinds of kaolinite (well and poorly crystallized), revealing that poorly crystallized kaolinite was more reactive and promoted better mullitization. The samples with poorly crystallized kaolinite had porosities and shrinkages of 44% and 3.8%, whereas the well samples had porosities and shrinkages of 43% and 4.9%, respectively.

Surface diffusion refers to the process by which atoms or molecules migrate across the surface of solid materials, typically occurring at the boundaries between crystalline grains or on the

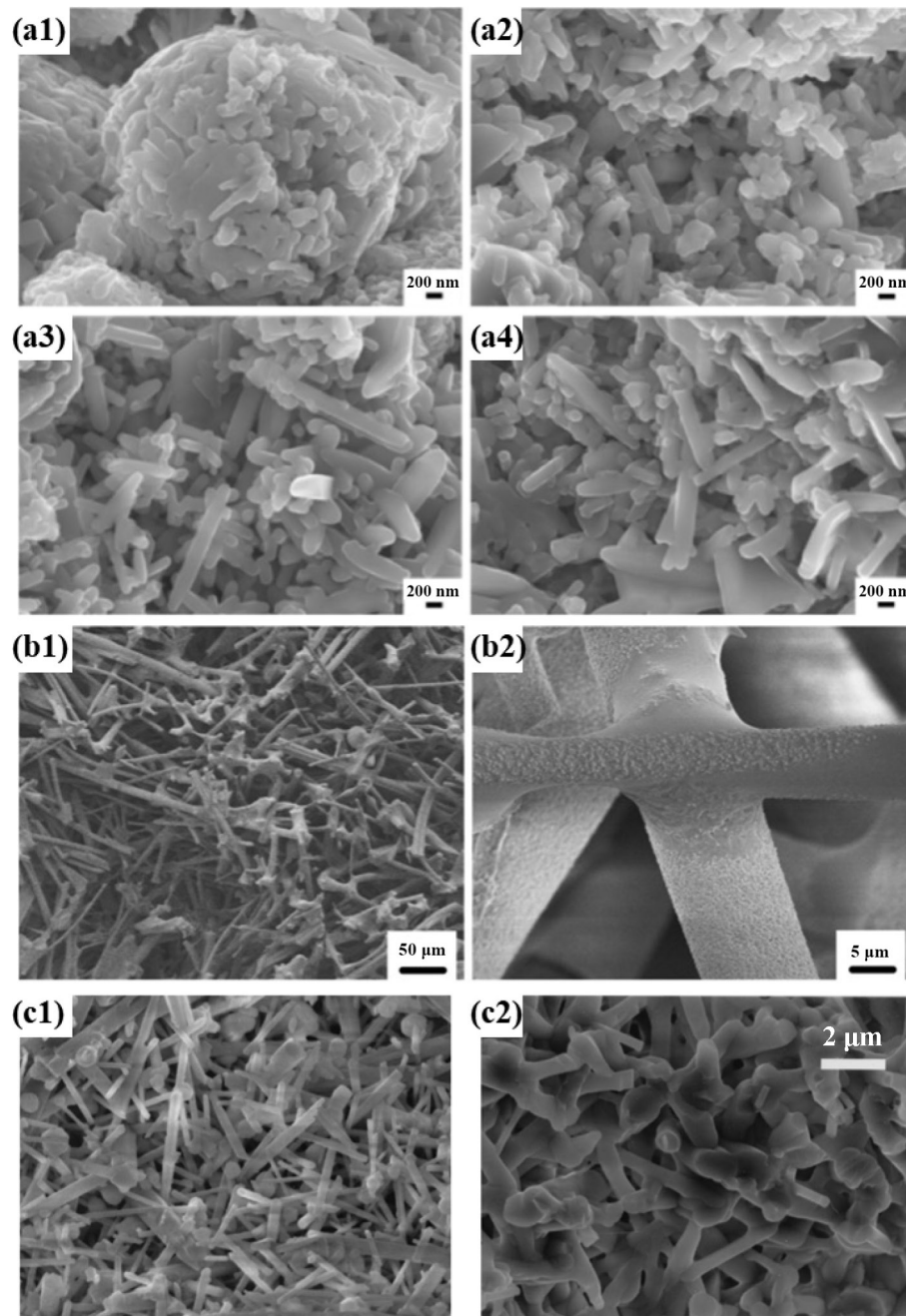


Fig. 16 SEM images of samples with (a) whiskers; (a1) M0, (a2) M5, (a3) M10, and (a4) M15 at a sintering temperature of 1200 °C. Reproduced with permission from Ref. [167], © Elsevier Ltd and Techna Group S.r.l. 2023. (b) Fibers, (b1) fibrous ceramics, and (b2) typical fibers nodes in fiber block sintered at 1500 °C. Reproduced with permission from Ref. [168], © Elsevier Ltd. 2015. (c) Porous Si_3N_4 ceramics sintered at (c1) 1750 °C and (b) 1850 °C. Reproduced with permission from Ref. [170], © The American Ceramic Society 2004.

surface of individual crystals. During solid-phase sintering, when surface diffusion is the primary mechanism of mass transport, it does not lead to sample shrinkage. This mechanism does not rely on the liquid phase and is only associated with factors such as the crystal structure, surface roughness, and atomic interactions. Compared with other materials, the sintering mechanism between SiC particles is surface diffusion due to its low self-diffusion coefficient and vapor pressure. In addition, Fukushima *et al.* [49] demonstrated the existence of an evaporation-condensation process through the stepping facets observed on the surface of SiC particles. Then, Fukushima *et al.* [157] obtained porous SiC ceramics using Al_2O_3 and Y_2O_3 as additives, which exhibited porosities ranging from 30.3% to 41.1% and shrinkages ranging

from 0.4% to 6.7%. Huang *et al.* [142] produced porous SiC ceramics via unidirectional freeze drying from SiC powders with two particle sizes. As the coarse particle content increased from 0% to 90%, the open porosity increased from 65.4% to 70.3%, whereas the shrinkage decreased from 1.35% to 1.05%. Generally, the specific surface area of large powder particles is smaller than that of small powder particles. Hence, coarse powders exhibit less sintering activity and weaken surface diffusion in sintering pores. In other words, the characteristics of mass transport are determined by the inherent properties and reactivity of the materials during solid-phase sintering.

The liquid phase can form a wetting layer between solid particles, reducing interparticle gaps, and facilitating particle

movement. It also acts as a flux, promoting a more uniform distribution and bonding of particles during sintering, which is detrimental to the formation of porous and low sintering shrinkage products. Ma *et al.* [172] used kaolin and α - Al_2O_3 as raw materials to prepare porous mullite ceramics with a shrinkage of -0.33% and a porosity of 68.44% . Ma *et al.* [172] subsequently explored the impact of boehmite sol on the reaction process and reported that the mullitization temperature was reduced to 900°C . Owing to more liquid phase present during sintering, the shrinkage of the sample with $25\text{ wt}\%$ boehmite sol increased to 0.18% . Evaporation-condensation diffusion is the process whereby atoms or molecules evaporate from a liquid phase into the vapor phase and then condense onto another surface where they recombine or form a new phase. This diffusion mechanism commonly occurs in vapor-phase deposition processes and plays a significant role in thin film growth and surface modification.

This principle stands in the fundamentals of sintering and mass transfer, analyzing the impact of the mass transfer process on shrinkage from the perspectives of particle rearrangement and grain coarsening. For the majority of mass transfer processes involving particle rearrangement, high reactant activity, low liquid phase formation temperatures, and increased liquid phase volumes all contribute to particle rearrangement, leading to shrinkage (however, for reactions that generate expansion phases, this effect is reversed, with the increased volume of new phases able to offset the shrinkage caused by sintering). Some mass transfer processes lead only to grain coarsening without causing shrinkage, such as surface diffusion and evaporation-condensation, which often occur in the sintering of low vapor pressure materials. Consequently, the shrinkage of SiC porous ceramics typically remains below 10% .

4 Typical low sintering shrinkage porous ceramics

4.1 Mullite-based ceramics

Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is the only stable compound in the Al_2O_3 - SiO_2 system and is known for its exceptional chemical stability, resistance to creep deformation, chemical corrosion resistance, high melting point, and low thermal conductivity, making it ideal refractory materials [173].

Table 6 summarizes the preparation methods, low sintering shrinkage principles, pore structures, and properties of low sintering shrinkage porous mullite-based ceramics (PMCs). The main low sintering shrinkage principles include the generation of expansion phases due to the mullitization reaction and the construction of a rigid skeleton. Low sintering shrinkage mullite with volume effects can be created from raw materials composed of Al and Si, such as kaolinite [153,171,172], kyanite [95,165,174], aluminum-silicon compounds [160], mullite seeds [175], and precursors [164,176]. Notably, some industrial waste, such as fly ash [134,167,177–180] and coal gangue [163,166], is recycled to produce mullite ceramics, which is an eco-friendly treatment. To increase porosity and reduce shrinkage, the whisker-growth promoters $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (MoO_3 precursor) [166], MoO_3 [95,172,176], AlF_3 [172,175], and V_2O_5 [178] were introduced to generate needle-like mullite whiskers. For mullite-based ceramics formed by a rigid skeleton, mullite fibrous ceramics fabricated by gel-casting constitute the majority, whereas various binders change the robustness of nodes and the stability of the skeleton [181–184]. Mullite powders are sometimes also utilized by foam-gelcasting to construct the particle skeleton [30,105]. The volume effect segregates the volume changes occurring during the

sintering process into two distinct phenomena. Shrinkage emerges as a compromise between the expansion induced by the formation of new phases and the shrinkage resulting from sintering, occasionally surpassing 8% [134,177]. Conversely, porous ceramics composed of mullite fibers or particles do not undergo an expansion phase. Instead, they rely on a rigid framework, and the inherently low resintering shrinkage to achieve reduced shrinkage, even falling below 1% [183–185].

The volume effect resulting from the mullitization reaction is a commonly used low sintering shrinkage principle. In the preparation process, additives such as MoO_3 , AlF_3 , and V_2O_5 , which lower the mullitization temperature, change the chemical composition of the amorphous phases, and promote the growth of mullite whiskers, are often introduced to increase the porosity and decrease the shrinkage rate of the samples. Additionally, they serve to enhance the mechanical properties through whisker reinforcement. Figure 17(a) shows a schematic of the firing process of porous mullite ceramics without and with MoO_3 . Xu *et al.* [176] prepared mullite samples with $10\text{ wt}\%$ MoO_3 , including an open porosity of 62.21% , a shrinkage of 1.80% , and a bending strength of 10.16 MPa . Figure 17(b) shows the growth mechanism of mullite whiskers with a MoO_3 catalyst, and Yan *et al.* [95] prepared porous ceramics with a mullite whisker network formed by first and second mullitization (Fig. 17(c)). Cao *et al.* [178] obtained porous mullite from recycled coal fly ash and natural bauxite with the addition of $3\text{ wt}\%$ V_2O_5 and $4\text{ wt}\%$ AlF_3 at 1400°C , which exhibited a porosity of 46.6% , shrinkage around zero, and a biaxial flexural strength of approximately 70 MPa .

Both mullite powders and mullite fibers can be directly used as raw materials to prepare low sintering shrinkage porous ceramics with low thermal conductivity owing to the stable structure formed by overlapping particles or fibers, along with their inherently low resintering shrinkage. Li *et al.* [187] prepared porous mullite ceramics with mullite micropowders as the raw materials and lignin fibers as pore-forming agents via gel-casting and investigated the impact of solid loading, temperature, and lignin fibers content on shrinkage and porosity. More solid loading results in a more stable skeleton, and a lower temperature diminishes mass transfer, while more pore-forming agents retain more pores after sintering, leading to a reduction in shrinkage and an improvement in porosity. Mullite ceramics with apparent porosities of 60.71% – 72.82% , shrinkage rates of 1.35% – 6.04% , and compressive strengths of 6.11 – 24.86 MPa at 1400°C sintering were subsequently obtained. With a matrix of mullite fibers and SiO_2 - B_2O_3 , Dong *et al.* [188] prepared fibrous mullite ceramics with high porosity (74.2% – 78.3%), low shrinkage (1.0% – 3.5%), low thermal conductivity (0.231 – $0.248\text{ W/(m}\cdot\text{K)}$), and high compressive strength (1.3 – 3.2 MPa).

4.2 Alumina-based ceramics

Al_2O_3 are important chemical engineering materials with high hardness, excellent insulation performance, and chemical stability. Table 7 summarizes the preparation methods, low sintering shrinkage principles, pore structures, and properties of low sintering shrinkage porous Al_2O_3 -based ceramics. Expansion due to the oxidation of Al powders is the most popular measure for producing low sintering shrinkage porous Al_2O_3 -based ceramics without shrinkage [154,195,196]. Excessive expansion should also be impeded. Therefore, Al_2O_3 was added to limit expansion [197,198]. Moreover, shrinkage can be regulated by changing the ratio of $\text{Al}_2\text{O}_3/\text{Al}$ and the shape and reaction activity of Al_2O_3 [199,200]. Owing to their main composition of Al and Al_2O_3 , secondary aluminum dross (SAD) and waste glass can be recycled

Table 6 Summary of features of low sintering shrinkage PMCs

Raw material	Additive	Fabrication method	Main low sintering shrinkage principle	Material	Porosity (%)	Shrinkage (%)	Mechanical strength (MPa)	Thermal conductivity (W/(m·K))	Ref.
Coal gangue, $\text{Al}(\text{OH})_3$	Whisker-growth promoter: $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	Dry-pressing	Expansion phase	Mullite-corundum	45–56	0–7.5	BFS: 25–32.5	—	[166]
High alumina fly ash	Whisker-growth promoter: MoO_3	Dry-pressing	Expansion phase	Mullite	48.00–49.90	-0.63–0.49	CS: 4.57–11.61	—	[167]
Kaolinite, alumina	Whisker-growth promoter: $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	Dry-pressing	Expansion phase	Mullite- Al_2O_3	43–44	3.8–4.9	FS: 36–47	—	[171]
Fly ash powders, bauxite	Whisker-growth promoter: AlF_3 , V_2O_5	Dry-pressing	Expansion phase	Mullite-corundum	35–50	-2–10	—	—	[178]
Tabular alumina, quartz, and fly ash floating bead	—	Dry-pressing	Expansion phase	Mullite-corundum	40–70	-4.5–7	CS: 30–130	—	[179]
Industrial waste fly ash, calcined high-Al bauxite powders	Sintering additive: titania	Dry-pressing	Expansion phase	Mullite	42.92–46.64	-1.5–2.0	FS: 28.27–34.54	—	[180]
Alumina, kaolin clay, Chinese clay, and Fe_2O_3	Pore-forming agent: rayon fibers	Pore-forming agent method	Expansion phase	Mullite	43.2–59.3	0.4–2.7	BS: 15.6–26.3	—	[153]
Coal gangue, bauxite	Pore-forming agent: corn starch	Pore-forming agent method	Expansion phase	Mullite-corundum	37.5–50	2–7	BFS: 75–120	—	[163]
Mullite precursor	Pore-forming agent: modified cenospheres	Pore-forming agent method	Expansion phase	Mullite	50.2	4	BFS: 45.9	1.28	[164]
Kyanite	Pore-forming agent: $\text{Al}(\text{OH})_3$	Pore-forming agent method, direct foaming	Expansion phase	Mullite-corundum	58.97–60.71	-1–3	FS: 7.72–9.63	—	[165]
Kaolin, $\alpha\text{-Al}_2\text{O}_3$, and boehmite	Whisker-growth promoter: AlF_3 , MoO_3 ; pore-forming agent: PS microspheres, starch particles	Pore-forming agent method	Expansion phase	Mullite-corundum	62.44–80.10	0.18–2.96	CS: 9.89–15.55	0.16–0.26	[172]
Mullite precursor	Whisker-growth promoter: MoO_3	Sol-gel	Expansion phase	Mullite	61.91	1.86	BS: 9.35	—	[176]
Kyanite, $\alpha\text{-Al}_2\text{O}_3$	Whisker-growth promoter: MoO_3	Gel-casting	Expansion phase	Mullite- Al_2O_3	62.5–72.5	0.5–8	CS: 20–90	0.25–0.75 (0 °C)	[95]
Kaolin, $\rho\text{-Al}_2\text{O}_3$	Whisker-growth promoter: AlF_3 , $6\text{H}_2\text{O}$, MoO_3 ; pore-forming agent: carbon fibers	Gel-casting, pore-forming agent method	Expansion phase	Mullite	78.1–90.6	2–3	CS: 1.41–16.30	0.083–0.305	[158]
Mullite particles	Binder: $\rho\text{-Al}_2\text{O}_3$, polysilicon cutting waste; pore-forming agent: soluble starch	Gel-casting, pore-forming agent method	Expansion phase	Mullite	49.50–60	3.08–8.44	CS: 1.57–4.98	—	[189]
Kyanite	Whisker-growth promoter: AlF_3 ; foaming agent: SDS	Foam-gelcasting	Expansion phase	Mullite	79–87	3.5–9.0	CS: 1–8	0.1–0.5	[174]
Kyanite, Al	Whisker-growth promoter: AlF_3 ; foaming agent: SDS	Foam-gelcasting	Expansion phase	Mullite	81.5–86.4	-3.2–3.8	CS: 0.49–6.42	0.12–0.26	[190]
SiO_2 , Al_2O_3 , Al	Whisker-growth promoter: AlF_3 ; foaming agent: SDS	Foam-gelcasting	Expansion phase	Mullite	78.9–83.3	-5.2–0.3	CS: 0.51–1.02	0.24–0.29	[191]
Mullite seeds, CaCO_3 , $\alpha\text{-Al}_2\text{O}_3$, and SiO_2	Whisker-growth promoter: AlF_3 , $3\text{H}_2\text{O}$; foaming agent: SDS	Foam-freeze casting	Expansion phase	Mullite-anorthite	87.7–90.2	3.20–8.96	CS: 0.65–3.31	0.067–0.112	[175]

(Continued)

Raw material	Additive	Fabrication method	Main low sintering shrinkage principle	Material	Porosity (%)	Shrinkage (%)	Mechanical strength (MPa)	Thermal conductivity (W/(m·K))	Ref.
Al_2O_3 , ZrAl_3 , $\text{Al}_{75}\text{Si}_{35}$	—	Gel-casting, freeze drying, stereolithography	Expansion phase	Mullite- Al_2O_3 - ZrO_2	34.35	0	—	—	[160]
FAHSS, PAI2	—	SLS	Expansion phase	Mullite-cristobalite	83–87	3–8	CS: 0.5–2.5	0.1–0.3 (25 °C)	[177]
FAHSS, PAI2	—	SLS	Expansion phase	Mullite-cristobalite	57.7–62.4	7.2–9.8	CS: 2.50–4.86	1.12–1.21	[134]
Mullite fiber	Binder: zirconia sol	Sol-gel vacuum impregnation	Rigid skeleton	Mullite- ZrO_2	79.16–87.42	1.1–3.5	CS: 0.62–3.34	0.037–0.125	[155]
Mullite fiber	Binder: $\text{p-Al}_2\text{O}_3$, zircon; reinforcement: Y_2O_3	Gel-casting	Rigid skeleton	Mullite- ZrO_2	47–56	2.8–3.7	CS:10.5–14.5	0.75–0.87	[90]
Mullite fiber	Binder: silica	Gel-casting	Rigid skeleton	Mullite- SiO_2	75–78	2.5–5.0	CS: 1.6–2.8	0.12–0.24	[156]
Mullite fiber	Binder: silica	Gel-casting	Rigid skeleton	Mullite- SiO_2	71–75	1.3–2.8	CS: 1–13	0.17–0.22	[93]
Mullite fiber	Binder: silica resin, isopropyl alcohol	Gel-casting	Rigid skeleton	Mullite-cristobalite	81.6–82.3	1.8–2.8	CS: 1.21–1.58	0.083–0.089	[168]
Mullite fiber	Binder: silica sol, boric acid	Gel-casting	Rigid skeleton	Mullite- SiO_2 - B_2O_3	74.2–78.3	1.4–3.2	CS: 1.3–3.2	0.231–0.248	[188]
Mullite fiber	Binder: silica sol, aluminum phosphate sol	Gel-casting	Rigid skeleton	Mullite- SiO_2 - AlPO_4	77.4–78.6	1.1–2.5	CS: 1.1–2.1	0.157–0.165	[181]
Mullite fiber	—	Gel-casting	Rigid skeleton	Mullite- SiO_2	74.2–76.4	0.589–2.428	CS: 1.04–1.83	0.1165–0.1401	[182]
Mullite fiber	Binder: silica	Gel-casting	Rigid skeleton	Mullite- SiO_2	84.46–86.61	3.5–6.5	CS: 1.04–1.83	0.089–0.093	[29]
Mullite fiber	Binder: alumina, SiC; reinforcement: Y_2O_3	Gel-casting	Rigid skeleton	Mullite-corundum	61.1–71.1	1.36–3.08	CS: 4.4–7.6	0.378–0.467	[192]
Mullite fiber	Binder: kaolin, feldspar; pore-forming agent: corn starch	Pore-forming agent method	Rigid skeleton	Mullite-cristobalite	73.47–78.01	0.3–0.9	CS: 0.76–1.67	0.146–0.165	[183]
Mullite fiber, $\alpha\text{-Al}_2\text{O}_3$	Binder: kaolin, feldspar; pore-forming agent: corn starch	Pore-forming agent method	Rigid skeleton	Mullite- Al_2O_3	70.36	0.40	CS: 5.54	—	[184]
Mullite powders	Pore-forming agent: lignin fibers	Gel-casting, pore-forming agent method	Rigid skeleton	Mullite	60.71–72.82	1.35–6.04	CS: 6.11–24.86	—	[187]
Mullite powders	Foam agent: SDS	Foam-gelcasting	Rigid skeleton	Mullite-corundum	78–81	2.6–9.5	CS: 3.1–11.7	0.14–0.35	[193]
Mullite powders	Foam agent: SDS	Foam-gelcasting	Rigid skeleton	Mullite	64.2–75.7	1.46–3.47	CS: 7.90–26.62	0.279–0.598	[105]
Mullite powders	Foam agent: SDS	Foam-gelcasting	Rigid skeleton	Mullite	72.32–76.38	1.23–2.92	CS: 11.4–12.37	—	[30]
Mullite powder	Foaming agent: TLS; pore-forming agent: CaCO_3	Foam-gelcasting, pore-forming agent method	Rigid skeleton	Mullite-anorthite- Al_2O_3	72.98–79.07	2.35–4.83	CS: 5.52–14.82; FS: 2.5–5.5	0.114–0.247 (200 °C)	[194]
Firing-nonshrinkage clay, mullite fibers	—	Slip casting	Rigid skeleton	Mullite-corundum-anorthite	40–50	~0	BS: 39.8–57.9	—	[185]

Note: BFS: biaxial flexural strength; BS: bending strength; CS: compressive strength; FS: flexural strength.

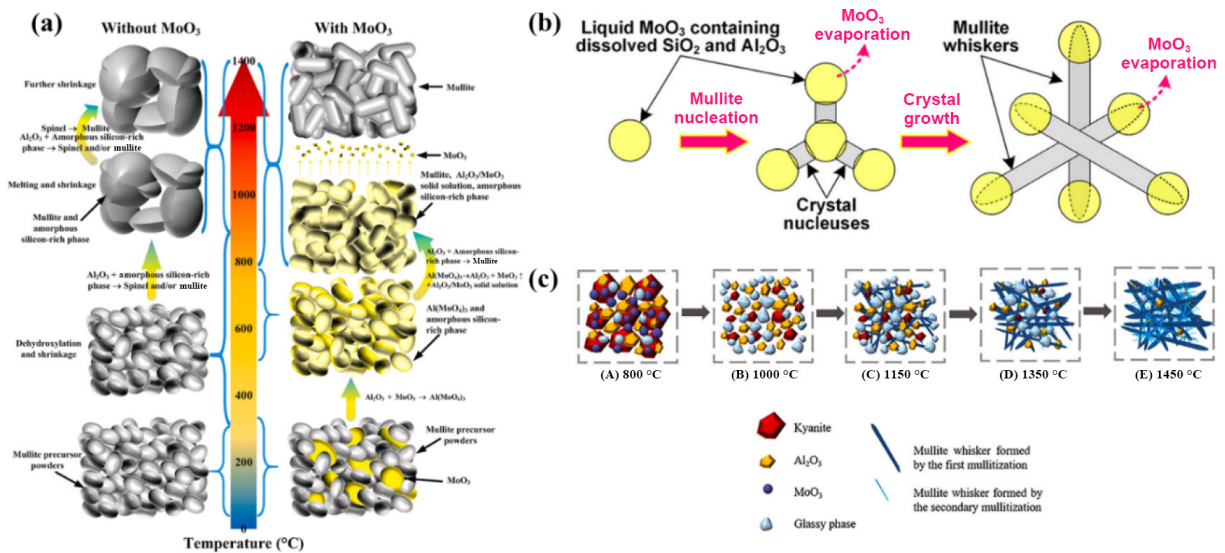


Fig. 17 Schematic illustration of (a) firing process of porous mullite ceramics without and with MoO₃. Reproduced with permission from Ref. [176], © Elsevier Ltd. and Techna Group S.r.l. 2021. (b) Growth mechanisms of mullite whiskers with MoO₃ catalyst. Reproduced with permission from Ref. [186], © American Chemical Society 2020. (c) Growth mechanisms of mullite whiskers formed by first and second mullitization. Reproduced with permission from Ref. [95], © The American Ceramic Society 2022.

Table 7 Summary of the features of low sintering shrinkage porous Al₂O₃-based ceramics

Raw material	Additive	Fabrication method	Main low sintering shrinkage principle	Material	Porosity (%)	Shrinkage (%)	Mechanical strength (MPa)	Ref.
Al powders	Foam agent: SDS	Direct foaming, gelation freezing	Expansion phase	Al ₂ O ₃	89.45–94.45	–4.31–5.88	CS: 0.35–2.19	[154]
Al powders	—	<i>In situ</i> hollow sphere	Expansion phase	Al ₂ O ₃ , Al/Al ₂ O ₃	~95	~0	—	[196]
Al powders	—	3D-printing	Expansion phase	Al ₂ O ₃	45.1–44.7	0.6–5.2	FS: 71.3–74.8	[195]
Fine and coarse Al ₂ O ₃ powders	Pore-forming agent: dextrin	Pore-forming agent method, SLA	Rigid skeleton, low mass transfer	Al ₂ O ₃	30.07	3.98	FS: 28.21	[206]
Al ₂ O ₃ powders	—	SLA	Rigid skeleton	Al ₂ O ₃	37.9	2.3–5.3	FS: 33.7	[50]
Al ₂ O ₃ powders	—	SLA	Rigid skeleton	Al ₂ O ₃	33.8	3.0–5.5	FS: 26.7	[207]
Al ₂ O ₃ powders	Pore-forming agent: CaCO ₃	DIW	Expansion phase	α-Al ₂ O ₃ , CA ₆ , and CA ₂	51.5–71.9	0.9–8.0	FS: 7.3–20.3	[204]
Al ₂ O ₃ , kaolin, MgO powders	—	DIW	Rigid skeleton, expansion phase	Al ₂ O ₃ –mullite	40.01	5.54	FS: 38.24	[31]
Al ₂ O ₃ , Al powders	Foam agent: SDS	Foam-gelcasting	Expansion phase	Al ₂ O ₃	86–92	–3–2	CS: 1.62–3.64	[197]
α-Al ₂ O ₃ , Al powders	—	<i>In situ</i> hollow sphere	Expansion phase	Al ₂ O ₃	30.69	–3.47	FS: 44.03	[198]
Spherical Al ₂ O ₃ , coral-like Al ₂ O ₃ , Al powders	—	SLS	Expansion phase	Al ₂ O ₃	57.6–73.7	0.52–7.04	BS: 0.78–7.37	[199]
Al ₂ O ₃ poly-hollow microspheres	—	SLS	Expansion phase	Al ₂ O ₃	77.09	6.63	CS: 0.18	[133]
α-Al ₂ O ₃ , Fe, Cu powders, and diatomaceous earth	Pore-forming agent: lignocellulose, carbon, and paraffin	Pore-forming agent method	Rigid skeleton, expansion phase	α-Al ₂ O ₃	40.22–52.25	–3.19–5.27	BS: 7.27–28.10	[200]
Al ₂ O ₃ , CaCO ₃ powders	Pore-forming agent method: PMMA	Gel-casting, pore-forming agent method	Expansion phase	α-Al ₂ O ₃ , CA ₆ , and CA ₂	58–66	1.4–7.3	CS: 5.9–15.5	[205]
SAD	—	Foaming and coagulation casting	Expansion phase	α-Al ₂ O ₃ , MgAl ₂ O ₄	36.34–43.49	1.38–3.60	FS: 4.35–28.25	[201]
SAD	—	High-temperature foaming	Expansion phase	Al ₂ O ₃	37.91	–1.13	FS: 45.67	[202]
SAD, waste glass	Foam agent: SDS	Direct foaming	Expansion phase	α-Al ₂ O ₃ , MgAl ₂ O ₄ , and Ca(Al ₂ Si ₂ O ₈)	87.3	6.56	—	[203]

to fabricate low sintering shrinkage Al_2O_3 -based porous ceramics, but the shrinkage rate remains below 7% [201–203]. Some additives can react with Al_2O_3 to form expansion phases, such as CaCO_3 transferred to calcium hexaluminate (CA_6) and calcium dialuminate (CA_2) [204,205], kaolin transferred to mullite [31], and MgO transferred to spinel [201]. When only Al_2O_3 powders are utilized as raw materials for AM, the primary principle of low shrinkage is attributed to the rigid framework formed by the Al_2O_3 grains. The porosity of those samples is approximately 30%, with a shrinkage of less than 5% [50,206,207]. Low sintering shrinkage porous Al_2O_3 -based ceramics can be obtained mostly by utilizing the Kirkendall effect of the Al powders. During the solid-state reaction or diffusion process, the diffusion rates of the atoms of two substances are different, leading to the formation of hollow particles. This phenomenon is called the Kirkendall effect and can be used to prepare metal oxide hollow spheres in air [208,209]. The Kirkendall effect of the Al powders not only causes significant volume expansion but also yields Al_2O_3 hollow spheres, increasing the porosity of the porous ceramics (Fig. 18(a)). Huo *et al.* [196]

established the colloidal assembly and oxidation of Al powders for the first time to prepare low sintering shrinkage porous ceramics via the Kirkendall effect. A stable foam slurry was obtained via the direct foaming method, and the composition, porosity, and shrinkage of the products were controlled by regulating the degree of oxidation of the Al powders. Furthermore, hierarchical porous Al_2O_3 and Al/ Al_2O_3 ceramics with porosities of up to 95% and nearly zero shrinkage were obtained. This colloidal assembly method was extended to fields such as 3D printing, freeze-casting, and gel-casting, demonstrating the application prospects of this system in the preparation of low sintering shrinkage porous ceramics with hollow Al_2O_3 particles (Figs. 18(b)–18(d)). Without pore-forming agents, porous ceramics can also be achieved via the *in situ* self-foaming of Al powders. Xia *et al.* [198] added Al powders with different particle sizes (50 nm, 1 μm , and 10 μm) to Al_2O_3 powders to investigate the effects of the Al powder content and size on the expansion effect. With increasing Al powder content, the shrinkage continuously decreases, and larger-sized Al powders can further reduce the shrinkage and yield larger pores.

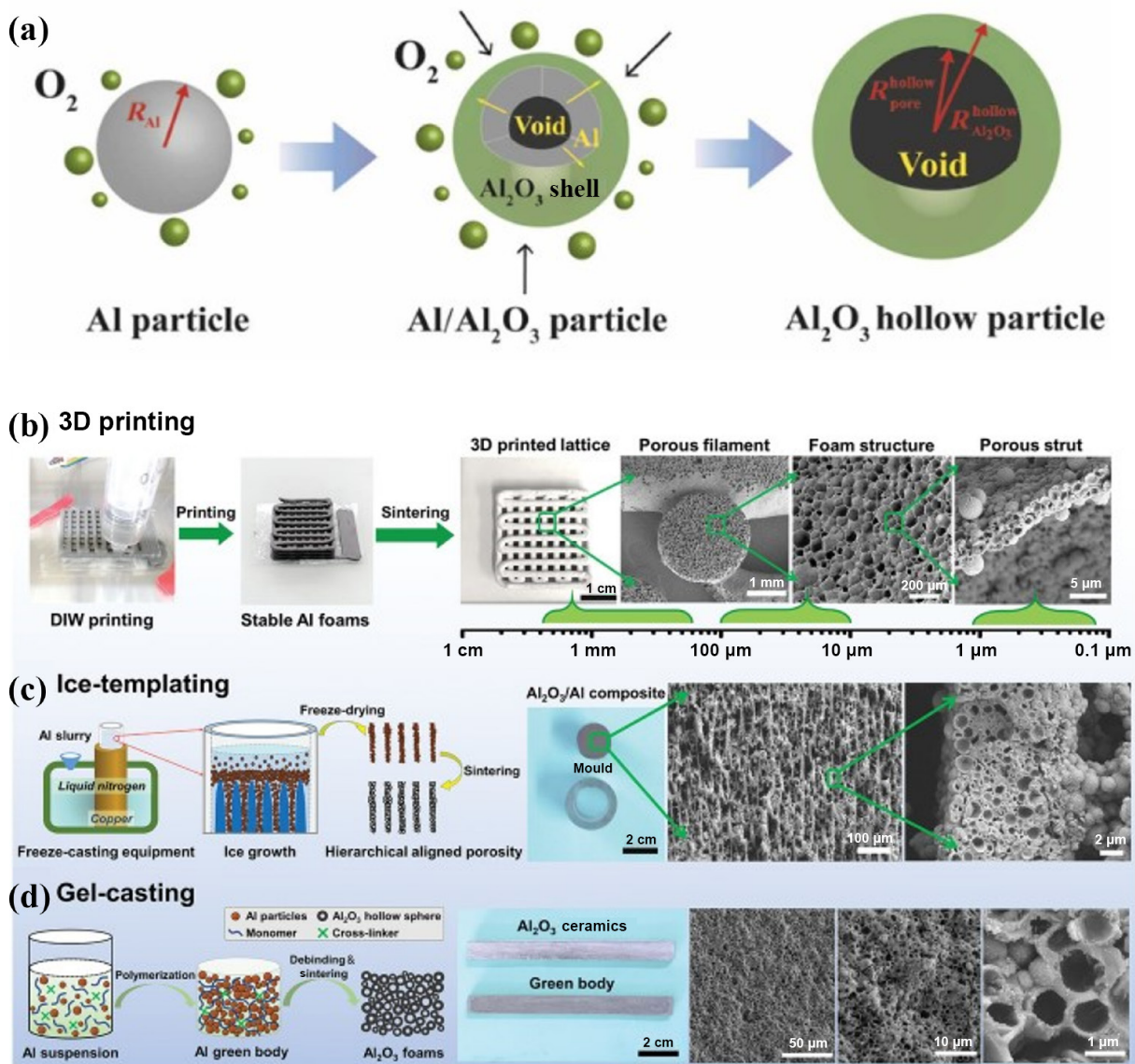


Fig. 18 (a) Schematic diagram of Kirkendall effect of Al powders. Reproduced with permission from Ref. [198], © Elsevier Ltd. 2023. (b) Colloidal assembly routes used to manufacture porous materials via thermal oxidation of Al particles, (b) 3D printing of Al wet foams, (c) freeze-casting, and (d) gel-casting. Reproduced with permission from Ref. [196], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2020.

When the addition amount of 10 μm Al powders was 50%, compared with that of the sample without Al powders, the shrinkage decreased from 16.45% to -3.47% , the apparent porosity increased from 2.5% to 30.69% due to the *in situ* hollow sphere method, and the flexural strength was 44.03 MPa.

Some low sintering shrinkage porous Al_2O_3 -based ceramics were prepared via additive manufacturing of Al_2O_3 powders without expansion phases. Li *et al.* [207] obtained Al_2O_3 ceramic cores with a porosity of 33.8%, shrinkage of 3.0%–5.5% and flexural strength of 26.7 MPa via SLA of Al_2O_3 powders and a presintering process. The presintering process stabilized the structure of the green body, establishing a stable framework. As a result, the green body exhibited minimal sintering activity during subsequent sintering stages, leading to negligible shrinkage.

4.3 Silicon carbide/nitride-based ceramics

SiC and Si_3N_4 exhibit outstanding high-temperature stability, high hardness, excellent corrosion resistance, and substantial flexural strength and can undergo mutual transformation under certain

conditions. Low-shrinkage SiC/ Si_3N_4 ceramics are typically prepared by utilizing the low vapor pressure of SiC and the strong bonding between SiC and Si_3N_4 . The preparation methods, low sintering shrinkage principles, pore structures, and properties of low sintering shrinkage porous SiC/ Si_3N_4 -based ceramics are summarized in Table 8. These ceramics can be divided into SiC-based, Si_3N_4 -based, and SiC- Si_3N_4 -based ceramics, and each type presents unique low sintering shrinkage principles.

The low shrinkage of the porous SiC ceramics with only SiC powders as raw materials is largely attributed to surface diffusion and evaporation–condensation mass transport occurring during the sintering process, as discussed in Section 3.3 [49,157]. A schematic of the principles and the stepping facets (highlighted in the yellow box) supporting the occurrence of the evaporation–condensation process is shown in Fig. 19(a). Li *et al.* [210] fabricated SiC- $\text{Al}(\text{PO}_3)_3$ porous ceramics via partial sintering with porosities ranging of 30%–38%, shrinkage rates ranging from 1.0%–1.8% and flexural strengths ranging of 25–27.5 MPa. A lower sintering temperature implies insufficient

Table 8 Summary of features of low sintering shrinkage porous SiC/ Si_3N_4 -based ceramics

Raw material	Additive	Fabrication method	Main low sintering shrinkage principle	Material	Porosity (%)	Shrinkage (%)	Flexural strength (MPa)	Ref.
β -SiC	α - Al_2O_3	CIP	Specific mass transfer	SiC	35–45	0–4	—	[49]
β -SiC	α - Al_2O_3 , Y_2O_3	CIP	Specific mass transfer	SiC	30.3–41.1	0.4–6.7	—	[157]
Fine and coarse SiC powders	B_4C	Unidirectional freeze casting	Specific mass transfer	SiC	64–72	0–2	—	[142]
SiC powders, aluminum dihydrogen phosphate	—	Partial sintering	Specific mass transfer, low mass transfer	SiC- $\text{Al}(\text{PO}_3)_3$	30–38	1.0–1.8	25–27.5	[210]
PCS precursors, graphene oxide	Pore-forming agent: PS microspheres	Pore-forming agent method	Expansion phase, rigid skeleton	SiC(rGO)	41.78–68.22	6.84–7.89	0.27–33.86	[218]
PCS precursors, PVG powders, and carbon fibers	—	Dry-pressing	Expansion phase, rigid skeleton	$\text{C}_f/\text{SiC}(\text{rGO})_{\text{px}}/\text{SiC}$	37.54–45.22	2.61–4.01	—	[211]
α -SiC powders, ground sieved fly ash	Pore-forming agent: PMMA, graphite; whisker-growth promoter: MoO_3	Pore-forming agent method	Expansion phase	SiC- SiO_2 -mullite	36.36–45.96	0.05–0.34	27.92–38.40	[219]
Si, α - Si_3N_4 powders	Y_2O_3	Dry-pressing	Expansion phase, rigid skeleton	β - Si_3N_4	51–56	2.8–3.4	84–151	[212]
Si, α -SiC powders	Y_2O_3	Freeze casting	Expansion phase, rigid skeleton	β - Si_3N_4	66.4–70.51	0.65–0.9	16.3–18.9	[141]
Si powders	Y_2O_3	Partial sintering	Expansion phase, rigid skeleton	α - Si_3N_4 and β - Si_3N_4	42.1–54.7	0.40–2.59	82–182	[213]
Si_3N_4 powders	Al_2O_3 , Y_2O_3	Partial sintering	Specific mass transfer, rigid skeleton	α - Si_3N_4 and β - Si_3N_4	45.8–59.5	2–6	57.6–175	[159]
Si_3N_4 powders	Silica gel	Sol-gel infiltration	Rigid skeleton	α - Si_3N_4 , β - Si_3N_4 , and α -cristobalite	33–43	~0	80–120	[214]
Si_3N_4 powders	Lu_2O_3	CIP	Rigid skeleton	β - Si_3N_4 , $\text{Lu}_4\text{Si}_2\text{O}_7\text{N}_2$, and Lu_2SiO_5	46–53	1–9	143–207	[214]
α -SiC powder with 6H polytype	Al_2O_3 , Y_2O_3	Unidirectional freeze casting	Specific mass transfer, rigid skeleton	SiC- Si_3N_4	32.61–63.41	0–1.94	6.8–164.3	[220]
Si_3N_4 powders	Pore-forming agent: carbon black, pure carbon	Pore-forming agent method	Rigid skeleton	SiC- Si_3N_4	40.4–58.3	1.26–3.54	~100	[170]
Si_3N_4 , carbon powders	Y_2O_3	Dry-pressing	Rigid skeleton	SiC- Si_3N_4	50–70	~1	20–100	[217]
Si, α -SiC powders	ZrO_2 , Y_2O_3	Partial sintering	Expansion phase, rigid skeleton	SiC- Si_3N_4	39.79–41.71	0.51–0.59	88.9–11.5	[215]
Si_3N_4 , ZrO_2 , H_3PO_4 powders	Pore-forming agent: starch	Pore-forming agent method	Rigid skeleton	Si_3N_4 - ZrP_2O_7	34.5–61.5	1.4–2.0	—	[221]
Si_3N_4 powders, silica sol	Al_2O_3 , Y_2O_3 ; Pore-forming agent: fly ash cenosphere	Gel-casting	Low mass transfer	Si_3N_4 - $\text{Si}_2\text{N}_2\text{O}$	36.7–53.1	0.2–5.7	45.1–180.5	[216]

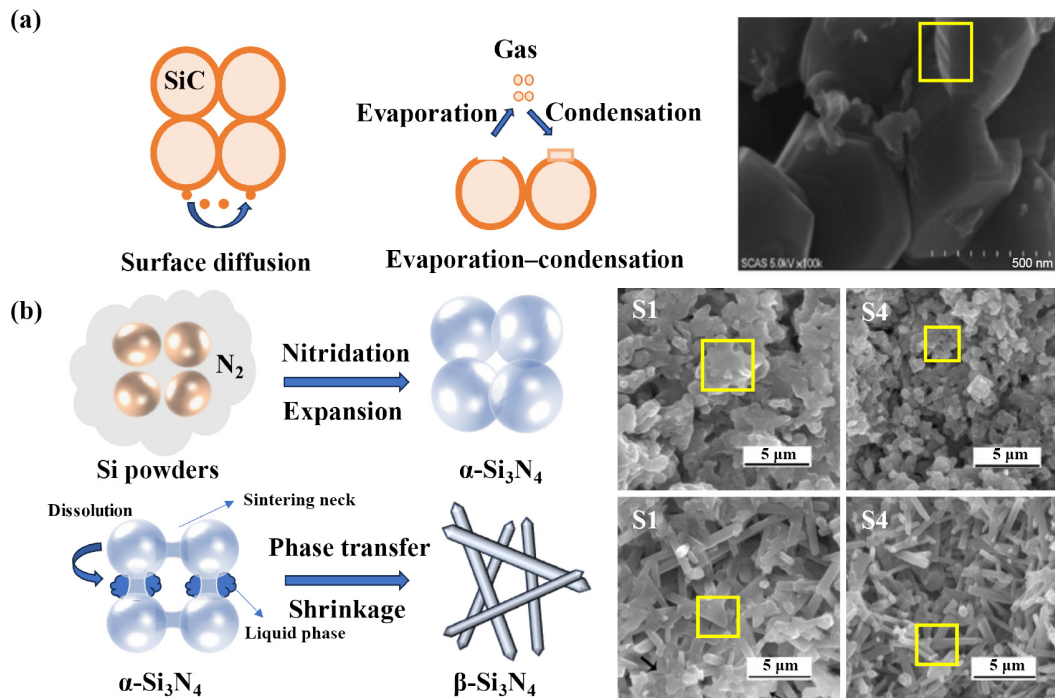


Fig. 19 (a) Schematic diagram of surface diffusion and evaporation-condensation processes. SEM image of porous SiC ceramics is reproduced with permission from Ref. [49], © The American Ceramic Society 2006. (b) Schematic diagram of nitridation and sintering process of porous Si₃N₄ ceramics. SEM images of samples S1 and S4 after nitridation and sintering are reproduced with permission from Ref. [213], © Elsevier Ltd. 2014.

mass transport, which can simultaneously increase the porosity and reduce shrinkage. For SiC-based ceramics created from polycarbosilane (PCS) precursors and additives, the low shrinkage below 8% resulted from the expansion of filler particles [142,211].

Si₃N₄ ceramics with low sintering shrinkage can be obtained mostly by volume expansion caused by the nitridation of silicon powders [141,212]. Yao *et al.* [213] reported that the degree of nitridation with decreasing Si particle size, owing to the increase in the reactive surface area and mass transfer process, resulted in Si₃N₄ ceramics with porosities ranging from 42.1% to 54.7%, shrinkages ranging from 0.40% to 2.59% and flexural strengths ranging from 82 to 182 MPa. Figure 19(b) shows the nitration of the Si powders and the phase transfer of α-Si₃N₄, and the SEM images prove that a greater degree of nitridation improved the degree of shrinkage. Smaller particles imply more aggregation of the liquid phase at the sintering neck (highlighted in the yellow box), leading to dissolution and rearrangement of the grains at the neck. Shrinkage occurs as α-Si₃N₄ dissolves, ceasing when the liquid phase saturates and begins forming a sufficiently strong rod-like β-Si₃N₄ phase. Compared with the sample S4 (shrinkage of 2.33%), the sample S1 exhibited strong sintering necks and hence experienced a decrease in shrinkage of 0.40%. For those Si₃N₄-based ceramics without silicon powders, the low shrinkage is attributed to the strong neck growth between the nitrided particles, hindering capillary forces to rearrange in liquid sintering, and the shrinkage ranges from 0% to 9% [159,214].

For porous SiC-Si₃N₄ ceramics, the strong bonding between SiC and Si₃N₄ increases the difficulty of green body shrinkage, while the formation of secondary phases also impedes mass transport and particle rearrangement, thereby reducing shrinkage [170,215,216]. Yang *et al.* [217] obtained porous SiC-Si₃N₄ ceramics via a carbothermal reaction between Si₃N₄ and carbon, resulting in high porosity (50%–70%), low shrinkage (~1%), and excellent flexural strength (20–100 MPa).

4.4 Other ceramics

In addition to the above material systems, several low sintering shrinkage ceramics have been manufactured via the expansion phase or rigid skeleton structures. The preparation methods, low sintering shrinkage principles, pore structures, and properties of those ceramics are summarized in Table 9. For materials with volume effects, the phase transfer of SiO₂ [222,223] and the expansion accompanied by the generation of spinel [224], cordierite [225,226], and ZrB₂ [162] were considered. The main materials with rigid skeletons include SiO₂ fibers [169], a TiB₂-TiB whisker framework [161], and a series of Y₂SiO₅/Y₂Si₂O₇ [89,227–232].

Using the SLA process, Li *et al.* [222] prepared silica ceramics with porosities ranging from 33% to 44% and shrinkage rates ranging from 1% to 6%, which was attributed to volume expansion during the phase transformation from α-cristobalite to β-cristobalite. Using MgO, Al₂O₃, and SiO₂ as raw materials and foam-gelcasting, Li *et al.* [226] obtained porous cordierite with a porosity of 82.49%–89.18% and a shrinkage of –1.40%–1.43%, owing to the bulk expansion accompanying the generation of cordierite. Wu *et al.* [227–230,232] fabricated a series of low sintering shrinkage porous Y₂Si₂O₇-based ceramics by constructing a rigid skeleton, demonstrating the existence of strong sintering necks to prevent shrinkage.

5 Potential applications

Porous ceramics have a wide range of applications because of their unique pore structures, and low sintering shrinkage contributes to maintaining the structural stability and precision of the products, which is highly important for industrial production. Figure 20 illustrates the potential applications of low sintering shrinkage porous ceramics. The primary direction for the development of low sintering shrinkage porous ceramics is demand oriented, with a focus on adjusting sintering shrinkage, porosity, and pore

Table 9 A summary of features of several low sintering shrinkage porous ceramics

Raw material	Additive	Fabrication method	Main low sintering shrinkage principle	Material	Porosity (%)	Shrinkage (%)	Compressive strength (MPa)	Thermal conductivity (W/(m·K))	Ref.
Silica fibers	Binder: BN, potato starch	Press-filtration	Rigid skeleton	SiO ₂	93.5	0	0.7	—	[169]
SiO ₂	—	Gel-casting	Expansion phase	Cristobalite	32.8	1.98	—	—	[233]
SiO ₂	Al ₂ O ₃	Stereolithography	Expansion phase	α-cristobalite, β-cristobalite, and quartz	33–40	1–6	—	—	[222]
Quartz glass powders	ZrO ₂ , carbon fibers	Injection molding	Expansion phase, low mass transfer	ZrSiO ₄ , SiO ₂ , and SiC	34–44	0.4–1.8	—	—	[223]
Al, MgO	Foam agent: SDS	Direct foaming	Expansion phase	MgAl ₂ O ₄	92.86–94.25	1.9–5.21	2.95–4.17	—	[224]
MgO, Al ₂ O ₃ , and SiO ₂	Foam agent: SDS, lauryl alcohol	Foam-gel casting	Expansion phase	Cordierite	82.49–89.18	–1.40–1.43	0.91–4.18	—	[226]
MgO, Al ₂ O ₃ , and SiO ₂	Fe ₃ O ₄	Foam-gel casting, freeze drying	Expansion phase	Cordierite, Mg–Al–Fe spinel	83.9–88.3	2.15–5.05	1.46–2.65	—	[225]
Slags, colloidal silica	Foam agent: CTAC	Direct foaming	Low mass transfer, rigid skeleton	Anorthite ((Ca,Na)(Si,Al) ₄ O ₈), augite (Ca(Fe,Mg)Si ₂ O ₆ , and (Fe,Mg,Ca)SiO ₃)	74.67–83.4	5.48–8.57	1.0–4.01	0.1031–0.2151	[234]
ZrO ₂ , B ₄ C	Pore-forming agent: carbon black	Partial sintering, pore-forming agent method	Low mass transfer	ZrB ₂	65–72	0.5–7.9	3–28	3–9	[162]
TiB ₂ , Ti	—	Freeze-drying	Low mass transfer, rigid skeleton	TiB–TiB ₂	72.1–77.1	1.6–2.2	1.8–18.2	—	[161]
Y ₂ O ₃ , SiO ₂	Carbon fibers	Gel-casting	Rigid skeleton	Y ₂ SiO ₅	73.94–87.71	0.48–6.13	0.30–3.29	0.051–0.134	[89]
Y ₂ O ₃ , SiO ₂	Foam agent: SDS	Foam-gelcasting	Rigid skeleton	Y ₂ SiO ₅	60.7–88.4	4.5–6.3	0.90–38.2	0.126–0.513	[231]
Y ₂ O ₃ , SiO ₂	Foam agent: SDS	Foam-gelcasting	Rigid skeleton	γ-Y ₂ Si ₂ O ₇	84.9	6.0	6.22	0.230 (30 °C)	[228]
Y ₂ O ₃ , SiO ₂	Foam agent: SDS	Foam-gelcasting	Rigid skeleton	γ-Y ₂ Si ₂ O ₇	57.2–90.0	6.1–9.9	3.4–46.5	0.147–0.918 (30 °C)	[230]
Y ₂ O ₃ , SiO ₂	YSZ fibers; Foam agent: SDS	Foam-gelcasting, freeze drying	Rigid skeleton	γ-Y ₂ Si ₂ O ₇ -YSZ	92.7–93.5	6.6–9.2	0.99–1.36	0.090–0.107	[227]
Y ₂ O ₃ , Ho ₂ O ₃ , and SiO ₂	Foam agent: SDS	Foam-gelcasting	Rigid skeleton	γ-(Y _{1-x} Ho _x) ₂ Si ₂ O ₇	79.3–81.2	4.7–7.2	11.0–13.9	0.186–0.309 (30 °C)	[229]
Y ₂ O ₃ , Ho ₂ O ₃ , and SiO ₂	YSZ fibers; Foam agent: SDS	Foam-gelcasting	Rigid skeleton	γ-(Y _{0.8} Ho _{0.2}) ₂ Si ₂ O ₇ -YSZ	93.2	7.1	1.2	0.077	[232]

structures to meet specific application requirements. For example, in the field of thermal insulation, a high porosity combined with the low thermal conductivity of a material enhances the thermal insulation performance of ceramics [235]. In the filtration industry, porous ceramics, with their stable corrosion resistance and high melting points, can be effectively utilized for filtering molten metals. The interconnected pore structures facilitate the passage of liquid or gas phases, and the filtration efficiency can be optimized by controlling the pore size [236]. Furthermore, low sintering shrinkage porous ceramics present broad application prospects in the preparation of ceramic cores. Ceramic cores often require precise shaping for complex geometries; if the shrinkage is too high, it may lead to dimensional changes in the core, thereby affecting the dimensional accuracy and shape stability of the final product [237]. Similarly, bioceramics used for bone repair require high structural stability, necessitating that the shape and dimensions of the ceramic materials conform to the intricate structures of bones. By designing porosity and strength appropriately, porous ceramics can achieve mechanical properties

close to those of natural bone and are capable of bearing loads within the biological environment and supporting the delivery of bioactive substances [238].

In summary, low sintering shrinkage porous ceramics demonstrate exceptional performance across various application fields. Their low sintering shrinkage characteristics not only ensure dimensional accuracy and stability during processing and usage but also enhance the overall reliability and durability of the materials. This highlights the significant development potential of low sintering shrinkage porous ceramics as a highly attractive research and application direction in modern industry and biomedical fields.

5.1 Thermal insulation

Conduction is the dominant heat transfer mechanism, whereas convection and radiation mechanisms only take effect at high temperatures [55]. Ceramic foams can be perceived as composite structures comprising ceramic skeletons interspersed with pores filled with air; the air functions as an integral insulation phase,

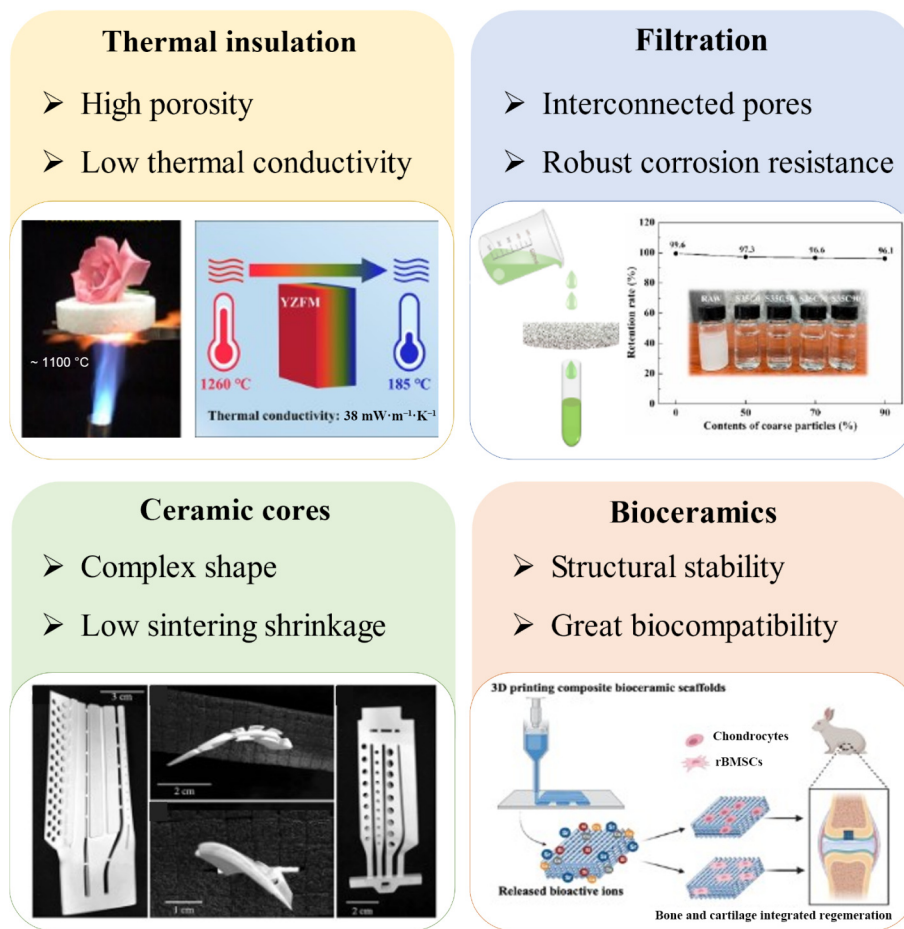


Fig. 20 A schematic diagram of potential applications of low sintering shrinkage porous ceramics. Images of thermal insulation are reproduced with permission from Ref. [239], © American Chemical Society 2019; Ref. [240], © Elsevier B.V. 2021. Image of filtration application is reproduced with permission from Ref. [142], © Elsevier Ltd and Techna Group S.r.l. 2021. Image of ceramic cores is reproduced with permission from Ref. [206], © Elsevier Ltd and Techna Group S.r.l. 2022. Image of bioceramics is reproduced with permission from Ref. [241], © The Authors 2023.

significantly contributing to the lower thermal conductivity of the foam ceramics. Five common thermal conductivity theoretical models for two-component materials are summarized in Fig. 21 [242]. All the theoretical models indicate that the thermal conductivity decreases with increasing porosity. Even though the relationship between porosity and sintering shrinkage is not necessarily linear, reducing sintering shrinkage under a constant solid phase mass can generally effectively increase porosity. The interparticle contact and the formation of the liquid phase during sintering contribute to shrinkage. When the shrinkage rate decreases, the gaps between particles are more likely to be maintained, allowing more pores to remain unfilled or open. This means that upon completion of sintering, a greater number of pores are preserved, leading to an increase in porosity. Therefore, inhibiting sintering shrinkage is an effective way to reduce the thermal conductivity by increasing the porosity.

Owing to its high creep resistance, low thermal conductivity, excellent corrosion resistance, and thermal shock resistance, mullite has garnered extensive application and research attention in thermal insulation [243]. Lin *et al.* [174] produced mullite ceramics with an increase in porosity from 75.2% to 86.3% and a decrease in thermal conductivity from 0.57 to 0.19 W/(m·K). In addition, for the high-temperature resistance of the sample with 85.2% porosity, the maximum temperature of the hot side reached 1172 °C while the cold side was only 464 °C after 240 s of heating.

Yuan *et al.* [192] fabricated porous fibrous mullite ceramics with desirable properties for high-temperature applications

through an epoxy resin gel-casting process. Tailored porous ceramics exhibit low linear shrinkage (1.36%–3.08%), high porosity (61.1%–71.7%), enhanced compressive strength (4.4–7.6 MPa), and low thermal conductivity (0.378–0.467 W/(m·K)), making them promising candidates for thermal insulation and hot gas filtration. Yan *et al.* [95] presented the near-net-size fabrication of porous mullite ceramics with high strength and porosity, achieved through gel-casting and pressureless sintering, utilizing the *in situ* formation of a 3D mullite whisker network reinforced by MoO₃. The resulting porous mullite matrix ceramics demonstrate ultralow sintering shrinkage of 0.78%, high porosity of 63.9%, and enhanced mechanical properties (83.8 MPa compressive strength and 53.5 MPa flexural strength), offering potential for thermal insulation applications. Near-net-size sintering is facilitated by the 3D framework established by mullite whiskers, coupled with the expansion resulting from the decomposition of kyanite.

A novel approach for the coproduction of pure MoO₃ and PMCs has been developed through a single-step roasting process using industrial Mo calcine, kaolin clay, and alumina, achieving a high MoO₃ recovery efficiency of 95.71% [186]. The method uses MoO₃ as both a pore-forming agent and a crystallization catalyst, resulting in PMCs with excellent properties, such as high open porosity, low thermal conductivity, and good compressive strength, indicating great potential for use as thermal insulation materials. This new strategy offers a cost-effective and sustainable method for preparing PMCs and recovering MoO₃ with mutual

Model	Structure schematic	Effective thermal conductivity equation
Parallel model		$K = v_1 k_1 + v_2 k_2$
Series model		$K = \frac{1}{v_1 / k_1 + v_2 / k_2}$
Maxwell-Eucken 1 (k_1 = continuous phase, k_2 = dispersed phase)		$K = \frac{v_1 k_1 + v_2 k_2}{v_1 + v_2} \frac{3k_1}{2k_1 + k_2}$
Maxwell-Eucken 2 (k_1 = dispersed phase, k_2 = continuous phase)		$K = \frac{v_2 k_2 + v_1 k_1}{v_2 + v_1} \frac{3k_2}{2k_2 + k_1}$
EMT model		$v_1 \frac{k_1 - K}{k_1 + 2K} + v_2 \frac{k_2 - K}{k_2 + 2K} = 0$

Fig. 21 Five basic effective thermal conductivity structure models for two-component materials. Reproduced with permission from Ref. [242], © Elsevier Ltd and Techna Group S.r.l. 2016.

promotion and zero waste, addressing the challenges of environmental pollution and high costs associated with traditional methods.

In addition to mullite, other thermal insulator porous ceramics have also been explored. Borges *et al.* [244] investigated the impact of various calcium sources on the properties of alumina-based macroporous insulators and reported that the addition of CaCO_3 , Ca(OH)_2 , and CaO can reduce sintering temperatures and enhance insulating performance. The potential of *in situ* CA_6 formation to counteract shrinkage and lower the onset strengthening temperature contributes to high-temperature thermal insulators for industrial applications.

Lin *et al.* [245] presented the fabrication of lanthanum zirconate porous ceramics with high porosity and low thermal conductivity via a replica method, achieving excellent thermal insulation properties suitable for high-temperature applications. The resulting ceramics demonstrated a hierarchical pore structure, high porosity ranging from 87.6% to 96.0%, and adjustable thermal conductivity and compressive strength, indicating promising potential for thermal insulation in high-temperature environments.

Porous Y_2SiO_5 ceramics with low sintering shrinkage, high porosity, and high strength were fabricated via the *in situ* foam-gelcasting method [231], addressing the challenges of conventional fabrication techniques. Porous Y_2SiO_5 exhibited low thermal conductivity, maintaining over 95% and 80% of its room temperature strength at 1100 and 1300 °C, respectively, highlighting its potential as a high-temperature thermal insulator.

A one-step sintering method for producing porous ZrB_2 ceramics with tailored porosity and low thermal conductivity was presented, offering promising materials for thermal insulation applications [162]. Porous ZrB_2 ceramics synthesized through *in situ* boro/carbothermal reduction and partial sintering exhibit a homogeneous porous structure and mechanical properties that can be fine-tuned by varying the particle sizes of the starting

materials, offering a method to control the properties of porous ZrB_2 ceramics for thermal insulation applications.

In response to diverse application needs, porous ceramics characterized by minimal sintering shrinkage are extensively utilized for thermal insulation. To further improve the thermal insulation performance of ceramics, current developments include the study of medium/high-entropy ceramics [212], which involves a solid solution of multiple elements to increase the phonon-free path and change the intrinsic thermal conductivity of ceramics, thereby reducing the thermal conductivity of porous ceramics [213,214]. In addition, the thermal conductivity can also be decreased by optimizing the microstructure, such as by minimizing the grain and pore dimensions. Integrating these approaches with the low sintering shrinkage technique further enhances the thermal performance of porous ceramics.

5.2 Filtration

Porous ceramics are prized for their extensive utility in filtration applications, including hot gas filtration [246], diesel particulate filtration [247], and water treatment [248], owing to their exceptional attributes, such as an interconnected porous framework and robust corrosion resistance. The permeability coefficient directly affects the filtration effect of a sample. Low sintering shrinkage is beneficial for preserving the interconnected pore structure of a sample, thereby improving its filtration efficiency.

Huang *et al.* [142] utilized direction freezing casting to create SiC ceramic membranes with direction pores, and as the porosity increased from 65.4% to 70.3%, the permeability improved from 1.03×10^5 to $5.67 \times 10^5 \text{ L}/(\text{m}^2 \cdot \text{h})$ bar.

Fibrous porous ceramics are also suitable for filtration. Cuo *et al.* [183] fabricated fibrous mullite membranes with interconnected pores for dust removal, and the collection efficiency reached above 70% for dust particles of approximately 0.3–10 μm . The membranes exhibit low density, high porosity,

minimal linear sintering shrinkage, and low thermal conductivity, making them ideal for use in environments with high temperature and corrosive conditions. The ceramic membranes demonstrated excellent dust removal efficiency for fine particles and a low-pressure drop, highlighting their potential for application in gas filtration processes. The surface and cross-sectional morphology of the fabricated porous mullite ceramic membranes revealed a flat surface with no apparent holes or flaws, and the fibers were well welded together to maintain the mechanical strength. The microstructure shows a stable skeleton structure with interconnected channels and pores formed by the decomposition of corn starch, contributing to the high porosity of the ceramic membranes.

Guo *et al.* [165] fabricated porous mullite supports by casting and reaction sintering using the natural mineral kyanite as raw materials and $\text{Al}(\text{OH})_3$ as the pore-forming agent. The support exhibited high apparent porosity (58.97%–60.71%), a small average pore size (1.06–9.98 μm), excellent mechanical strength (7.72–9.63 MPa), and good nitrogen gas flux (4952–5322 $\text{m}^3/(\text{m}^2\cdot\text{h})$ at 0.4 MPa).

Guesmi *et al.* [249] prepared an alpha alumina-natural apatite-based porous ceramic membrane support via the extrusion method. The selected sample for filtration exhibited a porosity of 45.38%, a pore size of 1.35 μm , and a permeability of 959.64 $\text{L}/(\text{h}\cdot\text{m}^2\cdot\text{bar})$. Additionally, the sample displayed good chemical resistance, as evidenced by a weight loss of less than 1% in an acidic medium over one month.

For porous ceramic membrane supports, researchers have prepared porous ceramics with different microstructures. Furthermore, in addition to designing the microstructure of the sample, for membrane support, functional design can also be applied to porous ceramics, such as adding magnetic properties to enrich the functions of the ceramic membrane support [225]. Combined with near-net-size fabrication, the open pore structure of the green body could be preserved to the greatest extent possible, enhancing the filtration performance of the support.

5.3 Ceramic cores

Ceramic cores are essential components in the investment casting process, and hollow turbine blades are manufactured from investment-cast cores with complex shapes [250]. Ceramic cores should have excellent comprehensive properties, including low sintering shrinkage, thermal shock resistance, certain room- and high-temperature flexural strength [251]. The performance of ceramic cores directly affects the dimensional accuracy and properties of the final castings.

Multiple processes are used to prepare ceramic cores. For example, BaZrO_3 ceramic cores for high-temperature applications were fabricated via pressureless sintering [252]. The BaZrO_3 ceramic cores demonstrated excellent leaching characteristics in boiled dilute nitric acid, making them promising materials for use as core materials in the investment casting of hollow blades.

Currently, additive manufacturing is widely used to prepare ceramic cores. Specifically, low sintering shrinkage porous Al_2O_3 ceramics satisfy the requirements for cores applied to cast alloys with low sintering shrinkage, open porosity, and thermal stability. Tang *et al.* [206] produced alumina cores with a porosity of 30.07% and a shrinkage of 3.98% via SLA and achieved accurate formation. The results depict the complexity and precision achievable with the ceramic stereolithography 3D printing technique.

Alumina-based ceramic cores were fabricated via vat photopolymerization (VPP) 3D printing through *in situ* generation of YAG [253]. The addition of YAG significantly

reduces high-temperature deflection while maintaining high apparent porosity, which is crucial for the ceramic cores used in the investment casting of aeroengine turbine blades. The optimal process parameters were determined to obtain an excellent balance between high apparent porosity and low high-temperature deflection, providing valuable insights for the industrial application of 3D-printed ceramic cores.

The effects of sintering procedures and porosity on the properties of 3D-printed alumina ceramic cores were investigated [254]. A meticulous strategy has been devised to achieve 3D-printed ceramic cores with enhanced attributes tailored for high-temperature casting environments, integrating a pore-forming agent alongside a sophisticated triple-stage sintering process.

Silica-based ceramic cores reinforced with boron carbide (B_4C) were prepared through SLS and $\text{SiO}_2\text{-Al}_2\text{O}_3$ sol infiltration [255]. This research successfully produced complex-shaped silica-based ceramic cores with high mechanical strength and suitable porosity through combined SLS and sol infiltration, which can meet the requirements for high-temperature casting applications.

An approach for fabricating near-zero shrinkage alumina ceramic cores with excellent properties was presented [256], utilizing VPP 3D printing combined with atmosphere-controlled *in situ* oxidation of aluminum powders. The method significantly reduces linear shrinkage in the X direction to as low as 0.3%, and high apparent porosity (45.02%) and flexural strength (72.7 MPa) are achieved.

In summary, porous ceramics with different performances have been prepared and investigated to meet the usage requirements of ceramic cores. As precision criteria for ceramic cores, additive manufacturing, which aims to increase the dimensional accuracy of the cores and the ability to fabricate intricate structures, is an important development direction. This approach will propel the evolution of ceramic cores in the realm of precision casting toward a more integrated, intelligent, and high-efficiency manufacturing paradigm.

5.4 Bioceramics

Bioceramics exhibit high hardness and corrosion resistance and possess excellent biocompatibility and bioactivity, making them highly suitable for biomedical engineering applications. They are widely used in bone repair and dental implants, as they can integrate well with human tissues and promote bone regeneration and healing, establishing bioceramics as important materials in modern medicine [257]. The structure of porous bioceramics facilitates cell growth and nutrient exchange, and provides space for tissue development and the incorporation of bioactive substances, making them applicable in bone repair, tissue engineering scaffolds, and drug carriers [258].

Hydroxyapatite (HA) is a calcium phosphate bioceramic and primary mineral component of bone and teeth [259]. Porous HA ceramics with great mechanical strength are commonly used in bioscaffolds because of their similarity with human bones. Farhangdoust *et al.* [260] fabricated HA scaffolds by freeze-casting with a porosity of 76%, a compressive strength of 5.26 MPa, and a pore size of 88.4 μm . While the porosity of cancellous bone is in the range of 50%–95%, the macropores range from 320 to 1670 μm , and the compressive strength is in the range of 0.1–16 MPa [261–263]. The minimum acceptable pore size is approximately 100 μm ; however, to allow vascularization and new bone formation, pore sizes greater than 300 μm are suggested [264]. Thus, additive manufacturing is used to prepare porous HA ceramics with controllable unit structures. Feng *et al.* [265] produced porous HA ceramics with cubic pore units via DLP and

investigated the relationships among solid loading, porosity, shrinkage, and mechanical strength. The samples with lattice pore sizes of approximately 1 mm had porosities of 21.2%–36.5%, compressive strengths of 9.3–21.4 MPa, and shrinkages of 14.8%–21.6%. Although a reduction in porosity can enhance the mechanical strength of bioceramics, a greater porosity is beneficial for improving the permeability and degradability of scaffolds [266]. Therefore, balancing porosity and mechanical performance is an important topic in the preparation of porous scaffolds.

Si can be an essential element in human bone and bone growth and has a direct role in the mineralization of bone [267]. Si-based bioceramics have been investigated because of their bioactivity, excellent fracture toughness, and bending strength [268]. Porous CaSiO_3 -based bioceramics with a low shrinkage of approximately 8% were fabricated using 45S5 bioglass as the reinforcing phase and polyethylene glycol particles as pore-forming agents [269]. The bioceramics exhibited a high compressive strength of 20.33 MPa with an open porosity of 64.20%. However, the high mechanical strength mainly resulted from the unconnected pore structure. A series of CaSiO_3 bioceramics with different pore sizes and porosities were fabricated via 3D printing [270]. The pore size was controlled from 300 μm to 1 mm, and the porosity was 50%–70%. Compared with the CaSiO_3 bioceramics obtained by the pore-forming agent method, which have a high compressive strength, the scaffolds with an interconnected cubic pore size of 1 mm presented a compressive strength of 3.57 MPa with a porosity of 65% and demonstrated better *in vivo* osteogenic properties.

The rate and quality of bone integration are related to the pore size and interconnection size. Hence, structural stability is critical for bioceramic formation [271]. Excessive sintering shrinkage can affect the dimensional accuracy of the pore structure; thus, improving preparation methods to reduce sintering shrinkage and achieve precise shaping is also a developmental direction for porous bioceramics.

6 Summary and outlook

This paper reviews the fabrication methods, main principles, and potential applications of low sintering shrinkage porous ceramics. Low sintering shrinkage porous ceramics represent a novel class of materials with promising applications in various fields. They exhibit significant advantages in near-net-shape forming and precision manufacturing, offering potential reductions in waste generation during production processes, thus aligning with the development trend toward environmentally friendly chemical products. However, the field of low sintering shrinkage porous ceramics currently faces several challenges.

1) The selection of raw materials and preparation methods must align with the target products and technical specifications. Typically, mullite-based and alumina-based low sintering shrinkage ceramics are prepared via reaction sintering, accompanied by volume expansion. However, $\text{SiC}/\text{Si}_3\text{N}_4$ -based low sintering shrinkage porous ceramics capitalize on intrinsic mass transport properties. Notably, fiber-based porous ceramics are commonly fabricated via gel-casting to establish a fiber framework immobilized by binders aimed at hindering sintering shrinkage. Although high-entropy fibrous ceramics exhibit excellent performance in terms of porosity and thermal conductivity, they often suffer from high sintering shrinkage. Further research is needed to explore how to adjust the microstructure of the materials to achieve the goal of low sintering shrinkage. The material systems are relatively limited, with the application of volume effects not yet widespread, necessitating

broadening the utilization of raw materials associated with volume effects and diversifying material systems. Moreover, research on fiber-based ceramics remains relatively limited, demanding an expansion of both the selection and investigation of fiber-based materials. Among many fabrication techniques, AM stands out as an attractive method, integrating the mentioned material systems to achieve monolithic fabrication of low sintering shrinkage porous ceramics with multiscale pore structures and complex shapes.

2) The control and mechanism of drying shrinkage and the synergistic effect of drying and sintering shrinkage need to be explored. In the manufacturing process of porous ceramics, shrinkage and deformation mainly occur during the two stages of drying and sintering. It is necessary to comprehensively consider the effects of drying and sintering shrinkage and formulate reasonable production process parameters to ensure that the dimensional accuracy and shape stability of ceramic products meet the application requirements. Currently, research on the shrinkage of porous ceramics has focused mainly on the sintering stage. However, the shrinkage caused by drying is also highly important and cannot be ignored. On the one hand, deformation from drying leads to nonuniform pore structures. On the other hand, the stress generated during drying may interfere with the sintering process, thereby directly affecting the performance of porous ceramics. To effectively manage and control drying shrinkage, novel technologies such as vacuum freeze drying, microwave drying, and supercritical drying can be adopted.

3) The near-net shaping of large-scale components has received limited attention; thus, enlarging the material design dimensions and ensuring complete shaping represents a novel research direction in low sintering shrinkage ceramics. The preparation of large-sized and complex-shaped porous ceramics is a key technology for the industrialization of ceramic parts because of the sensitivity of ceramic materials to defects. The challenge in the preparation of large-scale components is mainly from the uneven temperature fields. For large-scale ceramics, heat conduction may not be uniform between the interior and surface of samples during sintering, which increases uneven deformation and even cracking. To achieve a uniform and efficient sintering of large-scale porous ceramics, the integration of advanced field-assisted sintering technology, such as microwave sintering and laser sintering, can be employed to produce low sintering shrinkage porous ceramics. These technologies can not only significantly improve the uniformity of the sintering process but also optimize the sintering efficiency by accurately controlling the energy input to meet the requirements of large-scale ceramic parts for high quality and performance. The application of innovative sintering technologies will open a new path for the preparation of low sintering shrinkage porous ceramics.

4) Porous ceramics with low sintering shrinkage can significantly maintain the uniformity of their pore structure owing to their small deformation. This advantage has been widely recognized and applied in the fields of thermal insulation materials, ceramic cores, and filter carriers. However, the potential application scenarios and scope of low sintering shrinkage technology need to be further expanded. On the basis of the low sintering shrinkage principles proposed in this article, expansion phases, rigid skeletons, and low-reactivity materials can be added to other ceramic systems as sintering shrinkage inhibitors to expand the application field of low sintering shrinkage porous ceramics. For example, in the field of bone tissue repair, the requirements for the dimensional accuracy of materials are particularly strict, as any small deviation may affect the repair

effect. The introduction of low sintering shrinkage principles into the preparation of bioceramics can achieve near-net-shaped sample formation, which will promote the application of bioceramics in the medical field. Therefore, broadening the application scope of low sintering shrinkage porous ceramics in diverse fields will play a positive role in promoting the progress of ceramic production.

5) For samples designed to achieve low sintering shrinkage through rigid structures or special mass transfer processes, volume shrinkage occurs only once during the sintering process, making it difficult to reduce the shrinkage rate to zero. In contrast, samples that achieve low sintering shrinkage through the expansion phase undergo at least two volume changes during sintering. For materials exhibiting reversible phase transitions, such as zirconia, the relationship between volume and temperature becomes more complex. When the volume expansion exceeds the sintering shrinkage, the product's shrinkage may drop below zero, even when it enters an expanded state. Throughout this volume change process, internal stresses may develop, which can affect the mechanical properties of the materials. However, questions remain regarding the existence of internal stresses in low sintering shrinkage samples via this principle, as well as the methods for quantifying these stresses and their mechanisms of action. Further research is needed to clarify these issues.

This review aims to guide the preparation of low sintering shrinkage porous ceramics, listing various methods for preparing low sintering shrinkage porous ceramics and focusing on the low sintering shrinkage principles of these ceramics as well as their potential applications and future outlook. The paramount significance of low sintering shrinkage lies in industrial fabrications, and further exploration of the industrial applicability and guiding significance of low sintering shrinkage porous materials holds critical importance, as this will drive scientific research toward a more practical and application-oriented trend. The development of technologies and equipment suitable for large-scale production is a significant task that drives the development of this field. Research on low sintering shrinkage porous ceramics involves multiple disciplines, such as material science, chemical engineering, and equipment manufacturing. Promoting the cross-integration of these fields will help address the challenges faced and drive innovation.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

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