Metal Zirconium Phosphate Macroporous Monoliths: Versatile Synthesis, Thermal Expansion and Mechanical Properties

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Abstract

A versatile synthetic method has been developed for the fabrication of metal zirconium phosphate (MZP) macroporous monoliths via a sol-gel process accompanied by phase separation. More than 30 kinds of MZP monolithic polycrystalline monoliths with co-continuous macroporous structure have been synthesized by simply adding the target metal salt in the starting solution with optimized compositions. Glycerol, due to its high boiling point, plays the key role as the solvent to prevent metal salt from recrystallization, allowing a homogeneous distribution of metal salts over the polymerizing zirconium phosphate network. Hierarchically porous polycrystalline strontium zirconium phosphate (SrZrP) monolith has been obtained when the dried gel was calcined at 800 °C. Very low thermal expansion (coefficient of thermal expansion (CTE) as $1.4 \times 10^{-6} \text{ K}^{-1}$) over a wide temperature range (38 °C to 1000 °C) together with good mechanical properties (flexural modulus as 8.0 GPa from 3 point bending test and Young's modulus as 1.9 GPa from uniaxial compression test) has been demonstrated, while high porosity (43 %) due to the presence of macropores reduces bulk density. As compared with dense ceramics of the same composition, the CTE value is lower and can be attributed to the presence of nanometer-sized small pores, which absorbs the anisotropic thermal expansion of each crystallite in the macropore skeletons at elevated temperatures.

Key words: Sol-gel, Metal zirconium phosphate, Hierarchical porosity, Ultralow thermal expansion, Mechanical property

1. Introduction

Porous materials are commonly found in our daily life as filters [1], heat/sound insulators [2], refractory [3], adsorbents [4] and artificial bone [5], and are gaining increasing importance in energy and environmental applications as electrodes [6], sensors [7], separation media [8], catalysts and catalyst supports [4, 9]. Among them, three-dimensionally continuous (co-continuous) macroporous monoliths (pore diameter > 50 nm) are attracting more and more attentions due to the enhanced flow-through property, especially when a pressure driven flow is applied. Not only the mass transfer in the monolith is accelerated, but higher efficiency for the reaction or interaction between the material and reactants than that of conventional fixed-bed reactor is observed with lower pressure drop [10-14]. In the past two decades, the methodology for the synthesis of co-continuous macroporous monoliths via the sol-gel process accompanied by phase separation has been established and successfully applied to different systems, such as inorganic oxides (ceramics) [15], organic polymers [16], and organic-inorganic hybrid systems [17]. However, as compared with other monolithic materials, few successes have been reported in the synthesis of co-continuous metal phosphates monoliths mainly due to their low solubility in aqueous medium. Instead of

homogeneous sol-gel transition to a monolithic gel, heterogeneous polymerization dominates and leads to precipitation in most cases. In recent years, we have successfully synthesized monolithic ceramics of calcium phosphate [18], lithium iron phosphate [19] and zirconium phosphate (ZrP) [20] with co-continuous macropores. As an important category of inorganic phosphate materials closely related to ZrP, MZP materials are widely used as solid-state electrolytes with high ion conductivity at relatively low temperatures [21], ion exchangers for solidification of nuclear waste [22] as well as ceramics with ultralow thermal expansion over a broad temperature range [23, 24]. Although solid-state synthesis is generally applied to obtain MZP ceramics, it usually requires high sintering temperature and finds difficulty in inducing high porosity (> 40 %) with controlled pore parameters. The sol-gel process is more cost-friendly, because the milder reaction conditions at lower temperatures can be employed in aqueous media. However, metal ions tend to be washed away or recrystallize into the original metal salts after the removal of solvent, causing serious inhomogeneity in the bulky ceramics. Tedious post treatments such as ball milling and high calcination temperature are generally required in order to obtain compositionally homogeneous materials.

Herein based on our previously reported synthetic method for ZrP [20], we introduce the versatile synthesis of more than 30 kinds of compositionally homogeneous polycrystalline MZP monoliths with co-continuous macroporous structure. Influences of the starting compositions and post heat treatment on the pore structure formation and crystal phase evolution are discussed with SrZrP as an

example. Effect of pore structure on the thermal expansion property and the mechanical property of the obtained SrZrP macroporous monoliths are studied.

2. Experimental

2.1 Reagents

Zirconium oxychloride octahydrate (Wako Pure Chemicals Ind., Ltd., Osaka, Japan) as the zirconium source and concentrated phosphoric acid (≥ 85 wt% in H_2O , Sigma-Aldrich Co. USA) as the phosphate source were used. A mixture of distilled water (Hayashi Pure Chemicals Ind., Co., Ltd., Japan), hydrochloric acid (Kishida Chemical, Japan) and glycerol (Kishida Chemical, Japan) was used as the solvent. Both poly(ethylene oxide) (PEO, average molecular weight 35,000, Sigma-Aldrich Co., USA) and polyacrylamide (PAAm, average molecular weight 10,000, 50 wt% in H_2O , Sigma-Aldrich Co., USA) were used as the phase-separation inducers. Metal sources were LiCl , NaCl , KCl , RbCl , CsCl , $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 , $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$, $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{TiOSO}_4 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich Co. USA).

2.2 Synthesis of MZP monoliths

MZP macroporous monoliths were synthesized based on our previous reported method [16]. In a

typical run, 1.29 g of zirconium chloride oxide octahydrate and an appropriate amount of metal sources (calculated based on the formula: $M_{1/n}^{n+}Zr_2(PO_4)_3$, M can be more than one kind of metal, n represents the valence state of the metal in the metal source) was dissolved in the mixture of 1.4 mL of 1 M hydrochloric acid aqueous solution and 1.6 mL of glycerol in a glass bottle. Predetermined amounts of PEO (W_{PEO}) and PAAm (W_{PAAm}) were then added to the solution (details are shown in Table S1). The mixture was kept stirred until a clear transparent solution was obtained, and the solution was then cooled at 0 °C in an ice-water bath. Then, 0.41 mL of concentrated phosphoric acid ($V_{H_3PO_4}$) that had been already cooled at 0 °C was added. The resultant solution was then kept stirred for 5 min, followed by gelation at 0 °C. The obtained wet gel was aged at room temperature for 5 h and dried at 60 °C for three days, followed by calcination at different temperatures.

2.3 Characterizations

Morphology of the fractured surface of the samples and the chemical composition were investigated by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS, JSM-6060S, JEOL, Japan). The crystal structure of the samples was confirmed by powder X-ray diffraction (XRD, RINT Ultima III, Rigaku Co., Japan) and high temperature XRD (SmartLab-SS, Rigaku Co. Japan, equipped with a high temperature control unit) using Cu K α ($\lambda = 0.154$ nm) as an incident beam. A platinum sample holder was used in high temperature XRD measurement and its position

was calibrated every time before measurement to eliminate the effect of thermal expansion of the platinum holder. Thermal properties of the samples were investigated by thermogravimetry-differential thermal analysis (TG-DTA, Thermal Plus TG 8120, Rigaku Co., Japan) with a continuous air supply at 100 mL/min. Meso- and microporous structure of the samples were characterized by nitrogen adsorption-desorption (BELSORP-mini II, Bel Japan Inc., Japan). Skeletal density and mechanical property of calcined gels were investigated with a helium pycnometer (ULTRAPYC 1200e, Quantachrome Corp., USA) and a material tester (EZGraph, Shimadzu Corp., Japan), respectively. Coefficient of thermal expansion was measured by thermal mechanical analysis (TMA-60, Shimadzu Corp., Japan) at a heating rate of 10 °C/min from ambient temperature to 1000 °C.

3. Results and Discussion

3.1 Synthesis of MZP monoliths

The starting compositions for synthesizing MZP monoliths are listed in **Table S1**. In our previous work, synthesis of ZrP porous monoliths with different molar ratios of zirconium to phosphorous was reported. Starting from zirconium and phosphorous molar ratio as 2:3, by simply changing the kind of metal salt added to the starting composition, altogether more than 30 kinds of MZP porous monoliths have been successfully synthesized with different metal species including mono-, di- and

trivalent metals as well as mixed metals with different molar ratios (**Table S1**). **Figure 1** shows SEM images and XRD patterns of the monovalent metal (Li, Na, K, Rb and Cs) ZrP porous monoliths calcined at different temperatures. Monoliths with co-continuous macroporous structure interconnected by polycrystalline skeletons corresponding to $MZr_2(PO_4)_3$ (M represents monovalent metal) were obtained. Similar results for di- and trivalent metals were shown in **Figure S1** and **S2**.

When metal salts dissolve in the solvent, hydrolysis occurs immediately, which releases a large amount of proton. Since the pH value of the solution is thus decreased, polymerization of metal species is largely inhibited. After all the starting reagents are mixed and a homogeneous solution is obtained, the polymerization between Zr species and phosphoric acid thus comes into domination. Simultaneously the polymers (PEO and PAAm) enhance phase separation with the progress of polymerization, and the transient structure of phase separation is frozen by the sol-gel transition, leading to the formation of such co-continuous macroporous structure. In the meantime, most of the other metals added remain dissolved in the solvent phase. After the evaporation of H_2O and volatile components such as HCl, the metal species were concentrated into glycerol and homogeneously distributed in the gel skeleton, which later diffused easily into the crystal lattice of ZrP at elevated temperature, giving rise to the MZP crystals. The difference in pH value after mixing all the starting reagents, which influences the kinetics of polymerization and thus the relative timing of phase separation and gelation of the solution, depends largely on the kind of added metal

salt. Furthermore, the interaction between polymers (PEO and PAAm) and the added metal species, such as the coordination interaction between transition metals and amide groups in PAAm, may influence the interaction between the polymers and the ZrP network, which thus changes phase separation tendency. Consequently, the gel formation occurs at different intermediate state of phase separation, which leads to the differences in macropore sizes (for example, **Figure S1 Mg, Ca, Sr** and **Figure S2 Al, Y, Fe**).

Such synthetic method was proven to be applicable also in multiple metals systems. The morphologies (**Figure S3** and **Figure S4**) and crystal structures (**Figure S3** and **Figure S5**) of obtained multiple metals ZrP macroporous monoliths are shown. Regardless of their valence states, metals can be homogeneously mixed at any ratios in the ZrP network with the macroporous structure maintained by the synthetic method we have developed, suggesting the versatility for the synthesis of macroporous ZrP-based monoliths with metal species across the periodic table. An exception for lithium sodium ZrP was observed due to the decrease of crystallization temperature when two metals were mixed, thus calcination at 800 °C led to the crystal growth which collapsed the macroporous structure. The homogeneity of the co-mixed metals in the ZrP network was indicated by the EDX mapping of the sodium strontium ZrP macroporous monolith with a Na/Sr ratio of 0.24:0.38 (**Figure S6**).

Since Zr is also tetravalent, it is reasonable to consider that Ti added here will occupy the same

lattice position as Zr. Therefore, instead of 2:3 as the starting molar ratio between Zr and P, 1:2 as the starting ratio between the total molar amount of Zr and Ti and the molar amount of P has been investigated. **Figure S7A** shows SEM images of pure zirconium pyrophosphate and titanium zirconium pyrophosphates with different Ti/Zr ratios. A drastic decrease of gelation time with increasing Ti/Zr ratio led to the freezing of the transient structure of phase separation at an earlier stage, where the compositional difference between the gel-rich phase and the solvent-rich phase is not large enough. As a consequence, gels with small macropores and diffusive interfaces were formed, and the further increase of Ti/Zr ratio led to the deterioration of co-continuous macroporous structure. When the molar ratio between Ti and Zr reached 0.3/0.7, gelation time was shortened to less than 1 min, making it very hard to control the gelation process. We therefore failed to obtain compositionally homogeneous macroporous monoliths when the molar ratio exceeded 0.3/0.7. **Figure S7B** shows the X-ray diffraction peaks at different planes of titanium ZrP porous monoliths with different Ti to Zr molar ratios after calcination at 1000 °C. As the amount of Ti increased, the diffraction peaks at each plane shifted to higher diffraction angle. Such results clearly indicate that Ti occupies the same lattice position as Zr, and since the size of Ti is smaller than Zr, the decrease of distance between planes could be speculated.

The tunability of macropore size of the obtained MZP monoliths is demonstrated in **Figure S8** with SrZrP as an example. Simply by changing slightly the amount of PEO, the phase separation

tendency can be changed; the more amount of PEO was added, the higher the phase separation tendency was, leading to the increase of macropore size.

3.2 Effect of Heat treatment

The crystallization process of MZP macroporous monoliths during heat treatment has been studied with SrZP as an example. **Figure 2** shows the SEM images of SrZP macroporous monoliths calcined at different temperatures. Macroporous structure were maintained even after calcination at 1000 °C. Results of TG-DTA are shown in **Figure 3A**. Endothermic peaks as well as the corresponding weight loss at temperatures lower than 100 °C and around 200 °C can be attributed to the evaporation of adsorbed water and glycerol as the solvent in the starting composition, respectively. The broad exothermic peak together with the weight loss starting from 250 °C to 500 °C is mainly due to the combustion of PEO and PAAm embedded in the gel skeleton as well as the decomposition of SrCl₂ as the Sr source. No mesopores or micropores were found in the monoliths heat-treated at temperature below 300 °C, while they started to appear when the heat treatment temperature was raised up to 300 °C with the BET surface area as 240 m²/g and mesopore size as 4 nm. As the temperature was further increased, the BET surface area and the pore volume start to decrease and the mesopore size increases. Pores with different sizes in the range of tens of nanometers were confirmed when the sample was calcined at above 800 °C, at which temperature,

the pure $\text{Sr}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ phase was formed (**Figure 3B, C, D, Table 1**).

Since glycerol is nonvolatile and has a high boiling point (290 °C), even after the evaporation of water during the drying process as well as the heat treatment at 120 °C, glycerol was still trapped in the gel network and acted as the solvent for SrCl_2 . Though it is difficult to incorporate Sr in the ZrP network due to the lack of strong interaction between them, the presence of glycerol in the gel network inhibits the precipitation and crystal growth of SrCl_2 , which leads to the homogeneous distribution of Sr in the monolith. However, the presence of glycerol in the monoliths heat-treated below 300 °C blocks the micropores and mesopores, as a result of which, no micropores or mesopores were found from N_2 sorption isotherms of those samples. Complete removal of glycerol was achieved after heat treatment at more than 300 °C, which was also confirmed by the appearance of both micropores and mesopores in the gel skeletons (**Figure 3C**). Due to the condensation of unreacted hydroxy groups in the monolith at high temperature (> 600 °C), shrinkage of the monolith started to occur with a decrease of total pore volume. Calcination at even higher temperature (> 800 °C) leads to the crystallization of the gel network. Mass transfer during this process as well as the tendency to decrease surface energy changed the nanoscopic morphology by eliminating micropores and small mesopores and yielding large mesopores. Larger nanometer-sized pores in the monoliths calcined at 800 °C (26 nm) and 1000 °C (140 nm) were formed as the interstitials between $\text{Sr}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ crystallites.

3.3 Thermal expansion and mechanical properties

Though several reports discussed from experimental results that porosity has no obvious effect on the CTE value of porous ceramics [25, 26], traditional synthetic methods for the generation of three dimensional pores in ceramics, such as gelate freezing, pyrolytic reactive sintering, addition of porogen (inert gas or polymers) and self-assembly, find their difficulty to maintain nanometer scale pores in the ceramic body after calcination at high temperature [27], where the drastic crystal growth commonly leads to densified skeletons. Hence, the effect of porosity at nanometer scales on CTE of bulky ceramics has yet to be thoroughly studied. In this research, except for the micrometer scale macropores, small macropores (66-140 nm) that are close to mesopore (2-50 nm) in size were found present in the case of SrZrP monolith even after calcination at 1000 °C. Such monolithic ceramic material with hierarchical porosity consisting of pure-phase crystallites is a matching candidate to study the effect of hierarchically porous structure on the bulk thermal expansion behavior.

Temperature-dependent bulk thermal expansion curves from TMA measurement for SrZrP monolith calcined at 1000 °C are shown in **Figure 4A**. The CTE value at the temperature range from 38 °C to 1000 °C was $1.4 \times 10^{-6} \text{ K}^{-1}$, lower than that of SrZrP dense ceramics ($2.2 \times 10^{-6} \text{ K}^{-1}$) synthesized via solid-state reaction and sintered under pressure at the same temperature range [28]

and can be classified as a material with ultralow thermal expansion ($\leq 2 \times 10^{-6} \text{ K}^{-1}$) [29]. As a comparison, further densified SrZrP monolith (higher skeletal density and bulk density, **Table 2**) with only micrometer scale macropores were prepared by calcination at 1100 °C and 1200 °C. The absence of nanometer scale macropores in those monoliths was confirmed from the very low N_2 adsorption volume shown in N_2 sorption isotherms **Figure S9**. The crystal size of the obtained monolith increased drastically from ~100 nm (1000 °C) to ~400 nm (1100 °C) and ~1 μm (1200 °C) as the calcination temperature was increased (**Figure 4B**) and the crystal structure remained as $\text{Sr}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ even after calcination at 1200 °C (**Figure S10**). Though the total porosity remained similar, the CTE value were found increased when the SrZrP monolith was calcined at higher temperature due possibly to the presence of those small macropores in the skeletons calcined at lower temperature (**Table 2**). Such small macropores formed via mass transfer and crystal growth from amorphous gel network during the calcination process, can act as a free space to effectively buffer the geometrical change of the microcrystals and the possible formation of microcracks, which otherwise cause the significant decrease of mechanical strength at elevated temperature.

An inflectional increase in the CTE value was observed at the range between 550 °C and 650 °C for the SrZrP monoliths calcined at different temperatures. Such thermal expansion behavior has not been reported in metal(IV) phosphate-based low thermal expansion materials. The irrelevance

of calcination temperature can exclude the crystal size and the pore structure as the possible reason for such behavior. Furthermore, no phase transition was observed from high temperature XRD patterns taken at this temperature range for the SrZrP monolith calcined at 1000 °C (**Figure S11**). Lattice parameters calculated from high temperature XRD patterns (based on R-3 space group, **Table S2**) revealed that the expansion of unit cell volume was partially responsible for the overall thermal expansion behavior. An increase in the a parameter was found much more significant at this temperature range as compared to that at 25 °C, while the c parameter remained almost unchanged, thus leading to the intense increase of unit cell volume.

Sufficient mechanical strength is always required for porous materials to be applied in a broader field. The mechanical properties of the SrZrP porous monoliths calcined at different temperatures were thus measured by uniaxial compression test and the results are shown in **Figure 4C** and **Table 2**. Increase of fracture strength (from 61 MPa to 115 MPa) as well as Young's modulus (from 1.9 GPa to 3.9 GPa) was observed as the calcination temperature was increased from 1000 °C to 1100 °C due to the further densification of the skeletons at higher temperature. However, the further increase in the calcination temperature to 1200 °C led to the intensive crystal growth, resulting in reduced interface between crystallites, which thus reduced the fracture strength of the porous monolith. The bending property was measured by 3-point bending on the SrZrP monolith calcined at 1000 °C (**Figure S12**). The fracture strength and the flexural modulus were calculated

to be 25 MPa and 8.0 GPa (strain range 0.1-0.2 %), respectively. With sufficient mechanical strength and low CTE, porous MZP monoliths synthesized from sol-gel accompanied by phase separation can be applied in broad fields where high dimension stability is required at high temperatures.

4. Conclusion

In this research, a versatile methodology for the synthesis of MZP macroporous monoliths has been demonstrated with various metal species including mono, di tri and tetravalent metals as well as mixed metals. A homogeneous distribution of the metals in the gel has successfully been achieved, because the presence of a small amount of glycerol as a solvent with high boiling point prevents metal salt from recrystallization during the drying process. The post-heat treatment at high temperature ($> 300\text{ }^{\circ}\text{C}$) removes glycerol from the colloidal ZrP network, which then yields mesopores, while further calcination at higher temperature ($\geq 800\text{ }^{\circ}\text{C}$) gives rise to crystallization of the gel network to polycrystalline MZP. The thermal expansion and mechanical properties have been studied on SrZrP as an example. Ultralow thermal expansion (coefficient of thermal expansion (CTE) as $1.4 \times 10^{-6}\text{ K}^{-1}$) over a wide temperature range ($38\text{ }^{\circ}\text{C}$ to $1000\text{ }^{\circ}\text{C}$) together with sufficient mechanical properties has been demonstrated (flexural modulus as 8.0 GPa from 3-point bending and Young's modulus as 1.9 GPa from uniaxial compression). As compared with dense

ceramics of the same composition, the lower CTE value is observed and can be attributed to the presence of nanometer-sized small pores in the macropore skeletons, which absorbs the anisotropic thermal expansion of each crystallite at elevated temperatures.

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Table 1 Pore characteristics of SrZrP monoliths heat-treated at different temperatures.

Temperature	$S_{\text{BET}} / \text{m}^2 \text{ g}^{-1}$	$V_{\text{p}} / \text{cm}^3 \text{ g}^{-1}$	D_{p} / nm
300 °C	240	0.17	4
600 °C	180	0.16	4
800 °C	33	0.10	11 / 26
1000 °C	5	0.05	66 / 140

Table 2 Mechanical and thermal expansion properties, skeletal and bulk densities of SrZrP monoliths calcined at different temperatures.

	Strength / MPa	^a E / GPa	^b CTE / 10^{-6} K^{-1}	^c ρ_s / g cm^{-3}	^c ρ_b / g cm^{-3}	Porosity / %
1000 °C	71	1.9	1.4	2.81	1.63	42
1100 °C	115	3.9	1.6	3.15	1.80	43
1200 °C	61	3.9	1.7	3.04	1.79	41

^a E represents Young's modulus calculated as $E = \text{stress} / \text{strain}$ at a strain range 0.1-0.2 %.

^b CTE represents coefficient of thermal expansion.

^c ρ_s and ρ_b represents skeletal density and bulk density, respectively.

Figure captions

Figure 1 SEM images and XRD patterns of monovalent metal (Li, Na, K, Rb, Cs) ZrP monoliths after calcination at 1000 °C for 2 h in the case of Li, Na, K, Rb and 800 °C for 2 h in the case of Cs (calcination at 1000 °C leads to the overgrowth of $\text{CsZr}_2(\text{PO}_4)_3$ crystals and deteriorates the macroporous structure).

Figure 2 SEM images of SrZrP monoliths heat-treated at different temperatures (120 °C, 200 °C, 300 °C, 600 °C, 800 °C, 1000 °C).

Figure 3 TG-DTA curves of SrZrP monolith heat-treated at 120 °C (A), XRD patterns (B), N_2 adsorption desorption isotherms (C) and BJH pore size distribution obtained from the adsorption branch (D) of SrZrP monoliths calcined at different temperatures.

Figure 4 Temperature-dependent bulk thermal expansion curves (A), SEM images (B) and stress-strain curves from uniaxial compression tests (C) of SrZrP monoliths calcined at different temperatures for 5 h.

Figure 1 SEM images and XRD patterns of monovalent metal (Li, Na, K, Rb, Cs) ZrP monoliths after calcination at 1000 °C for 2 h in the case of Li, Na, K, Rb and 800 °C for 2 h in the case of Cs (calcination at 1000 °C leads to the overgrowth of CsZr₂(PO₄)₃ crystals and deteriorates the macroporous structure).

Figure 2 SEM images of SrZrP monoliths heat-treated at different temperatures (120 °C, 200 °C, 300 °C, 600 °C, 800 °C, 1000 °C).

Figure 3 TG-DTA curves of SrZrP monolith heat-treated at 120 °C (A), XRD patterns (B), N_2 adsorption-desorption isotherms (C) and BJH pore size distribution obtained from the adsorption branch (D) of SrZrP monoliths calcined at different temperatures.

Figure 4 Temperature-dependent bulk thermal expansion curves (A), SEM images (B) and stress-strain curves from uniaxial compression tests (C) of SrZrP monoliths calcined at different temperatures for 5 h.

Graphical abstract