



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 1000 °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–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.

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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 [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

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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 H₂O, 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 H₂O, Sigma–Aldrich Co., USA) were used as the phase-separation inducers. Metal sources were LiCl, NaCl, KCl, RbCl, CsCl, MgCl₂·6H₂O, CaCl₂·2H₂O, SrCl₂·6H₂O, NiCl₂·6H₂O, CuCl₂·2H₂O, ZnCl₂, MnCl₂·4H₂O, CoCl₂·6H₂O, AlCl₃·6H₂O, YCl₃·6H₂O, CeCl₃·7H₂O, FeCl₃·6H₂O, LaCl₃·7H₂O, ErCl₃·6H₂O, TiOSO₄·xH₂O (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: $M_{1/n}^{n+} \text{Zr}_2(\text{PO}_4)_3$, 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 ($V_{\text{H}_3\text{PO}_4}$) 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). Fig. 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 $M\text{Zr}_2(\text{PO}_4)_3$ (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 H₂O 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

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