

Sol–gel synthesis of macroporous barium zirconate monoliths from ionic precursors via a phase separation route



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ABSTRACT

Monolithic macroporous barium zirconate derived from ionic precursors has been successfully prepared via a phase separation route in the presence of poly(ethylene oxide) (PEO) and propyleneoxide (PO). Poly(ethylene oxide) (PEO) acts as a phase separation inducer, while propyleneoxide (PO) acts as a gelation accelerant in the sol–gel process. Appropriate choice of poly(ethylene oxide) (PEO) and propyleneoxide (PO) allows the production of continuous macroporous monolithic gel with a porosity of ca. 63% and a macropore size of 1.8 μm . Some BaCl_2 recrystallizes in the dried gel, and subsequently tetragonal ZrO_2 phase precipitates after heat-treated at 800 $^\circ\text{C}$. The crystalline phase barium zirconate forms after heat treatment at 1100 $^\circ\text{C}$ in air, while the macroporous structure is preserved with a slight increase of porosity and a decrease of macropore size.

1. Introduction

Barium zirconate (BaZrO_3) is one of the excellent structural ceramic materials, and has been widely used as a high-temperature insulation material due to its good thermostability, low coefficient of thermal expansion and high mechanical strength [1–5]. Recently, barium zirconate was also applied in functional ceramic, fuel cells and catalysis fields because of other intrinsic properties, such as high dielectric constant, high proton conductivity with rare-earth doping and capability to generate hydrogen by water catalytic reaction [5–11]. Porous barium zirconate has larger specific surface area and lower density, which are expected to improve its application performances and broaden its application fields. However, there is no literature about preparation of porous barium zirconate materials.

The sol–gel process accompanied by phase separation is one of the synthetic methods to fabricate porous monoliths [4,12–15]. This technique provides an easy way to prepare well-defined hierarchical pore structures with continuous macropores in a monolithic shape under low-temperature wet chemical reaction [16–20]. The porous zirconia based monoliths such as macroporous zirconia monoliths, macroporous yttria-stabilized zirconia monoliths and porous $\text{La}_2\text{Zr}_2\text{O}_7$ monoliths have been successfully synthesized by this technique [21–23]. So far, there have been adequate theoretical justifications to account for the mechanism of porous monoliths preparations by the sol–gel process accompanied by phase separation. It is promising that more and more macroporous monolithic materials can be fabricated via this technique.

In this study, we successfully synthesized macroporous barium zirconate with continuous skeletons by means of sol–gel process accompanied by phase separation. The ionic precursors are utilized to synthesize barium zirconate monolith in the presence of poly(ethylene oxide) (PEO) and propyleneoxide (PO). The major analyses were focused on the influence of phase separation inducer and gelation accelerant on the morphologies of the monoliths, and the effect of the heat-treatment on the phase transformations and pore structures.

2. Experimental

2.1. Synthesis procedure

Zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, Aladdin, 99.9%) and barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, Aladdin, 99.95%) were used as precursors. Poly(ethylene oxide) (PEO, Aladdin) having average molecular weight (M_v) of 3×10^5 was used as a phase-separation inducer, and ethylene glycol (EG, Sinopharm Chemical Reagent, 99.5%) was used as complex agent. Formamide (FA, Sinopharm Chemical Reagent, 99.5%) was used to control the drying process, and propyleneoxide (PO, Aldrich, 99%) was used as a gelation accelerant.

For all the eight samples, the amounts of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, H_2O , EtOH, FA and EG are 1.610 g, 1.220 g, 6.6 ml, 3.6 ml, 0.2 ml and 0.4 ml, respectively. The variable reagents of barium zirconate gels prepared in this study are listed in Table 1. The sample gels were prepared as follows: $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and PEO

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Table 1
Variable compositions of different samples.

Sample	PEO/g	PO/mL	Gelation times
BZ1	0	0.36	5 h
BZ2	0.03	0.36	5 h
BZ3	0.10	0.36	5 h
BZ4	0.12	0.36	5 h
BZ5	0.10	0.0	Failed gelation
BZ6	0.10	0.20	8 h
BZ7	0.10	0.60	8 min
BZ8	0.10	0.70	5 min

were dissolved in a mixture of H₂O and EtOH under vigorous stirring at room temperature, and then EG was added into the mixture liquid. After 5 min, FA was added dropwise, then PO was added into the mixture liquid under 1 min stirring. The container together with the whole mixed solution was sealed and placed in 80 °C drying oven to gelate and age for 24 h. Then EtOH and a mixture of EtOH and TMOS were added into the container successively to exchange the solvent. After solvent exchange, the container was placed in 80 °C drying oven for 4–7 days to obtain dried gel.

2.2. Characterization of materials

Porous morphologies of as-prepared samples with different compositions were observed by a SU-70 scanning electron microscope (SEM, HITACHI Corp.). Powder X-ray diffractions (XRD) of the heat-treated as-prepared samples performed with Empyrean 200895 diffractometer (PANalytical B.V. Corp.) using Cu-K α radiation ($\lambda=0.154$ nm). The nitrogen adsorption–desorption of as-prepared samples were characterized by an Autosorb-1-C nitrogen adsorption–desorption apparatus (Quantachrome Corp.). Before each nitrogen adsorption–desorption measurement, the as-prepared samples were degassed at 200 °C under vacuum for more than 6 h. Specific surface area and pore size distributions were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH), respectively.

3. Results and discussion

3.1. Formation of macroporous morphology

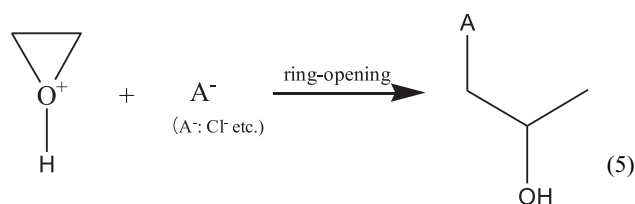
In the present system, zirconium oxychloride octahydrate (ZrOCl₂·8H₂O) and barium chloride dihydrate (BaCl₂·2H₂O) hydrolyze and polymerize together in the mixture of H₂O and EtOH to prepare homogeneous and transparent solutions. The PH of the solution declines to 2 after co-hydrolysis of two ionic precursors. The phase separation and gelation of the solutions can be controlled by the addition of poly(ethylene oxide) (PEO) and propyleneoxide (PO). The phase separation and gelation process can be described by Flory–Huggins formulation and ring-opening reaction as follows [24,25]. The Eqs. (1)–(4) come from Flory–Huggins formulation. χ_{12} is the interaction parameter, φ_i and P_i are the volume fraction and the degree of polymerization of component i ($i=1$ or 2), respectively, R is the gas constant, and T is the temperature. K_B is the Kauri-butanol parameter. As for the system Gibbs free energy change (Eq. (4)), the former term in parenthesis represent the enthalpic contribution (H), and the last two terms the entropic contribution (S) [16,26,27].

$$\Delta H = RT(\chi_{12}\varphi_1\varphi_2) \quad (1)$$

$$\chi_{12} \propto \frac{(\delta_1 - \delta_2)^2}{K_B T} \quad (2)$$

$$\Delta S = -R \left(\frac{\varphi_1}{P_1} \ln \varphi_1 + \frac{\varphi_2}{P_2} \ln \varphi_2 \right) \quad (3)$$

$$\Delta G = \Delta H - T\Delta S = RT \left(\chi_{12}\varphi_1\varphi_2 + \frac{\varphi_1}{P_1} \ln \varphi_1 + \frac{\varphi_2}{P_2} \ln \varphi_2 \right) \quad (4)$$



In this system, PEO has weak hydrogen bonds with inorganic oligomers and ethylene glycol (EG) complexing with Ba²⁺ inhibits the connection between PEO and oligomers, so PEO mainly distributes in liquid phase during the phase separation. With the increase of the degree of polymerization (P), the compatibility between oligomers and PEO chain reduces, which causes the decrease of system entropy change (ΔS) and the increase of system Gibbs free energy change (ΔG). When ΔG turns into positive, the system phase separation happens (Eq. (1)) [28,29]. When propylene oxide (PO) is added to the solution, PO captures the dissociated protons and conducts irreversible ring-opening reaction as shown in Eq. (2) [24,30], which drastically increases the pH of the solution from 2 to 4 and induces the gelation transition to form monolithic complex gels. The sol–gel process accompanied by phase separation of Ba–Zr–O system can be summarized in Fig. 1.

Fig. 2 shows SEM images of dried barium zirconate gels prepared with various PEO contents. The content of PEO used as a phase separation inducer determines the macroporous morphology of the gel. A dense monolithic gel sample without any clear pore structures is obtained when the PEO is not added (Fig. 2a). When the PEO content is 0.03 g, the as-dried sample shows some independent submicron pores but no continuous macropores and skeletons (Fig. 2b). When the PEO content increases to 0.10 g, continuous structures form with smooth skeletons and homogeneous macropores (Fig. 2c). The skeletons become thicker and the continuous structures are lost when 0.12 g PEO is added (Fig. 2d). As the phase separation inducer, different PEO contents prominently affect the phase separation tendency of the system and the morphology of as-dried samples.

Fig. 3 shows SEM images of as-dried barium zirconate gels prepared with various PO contents. The contents of PO used as a gelation accelerant determines macroporous morphology of the gels as well. There is no gelation transition in the system when PO is not added. When the PO content is 0.2 mL, the system becomes gel with course skeletons and no clear continuous structures in 8 h (Fig. 3a). When the PO content is 0.36 mL, the gelation transition takes place in about 5 h to form gels with continuous and homogenous skeletons (Fig. 3b). When the PO content is 0.5 mL, the system gels in 1 h, and the continuous skeletons become less obviously and the pore diameters become smaller (Fig. 3c). With the further increase of PO content to 0.6 mL, the system gels in only 5–8 min with the loss of skeletons and the transition of continuous pores into independent micron and nanoscale pores (Fig. 3d). As the gelation accelerant, the moderate PO content and the proper relative content of PEO are two key factors on the formation of interconnected macroporous barium zirconate gels with continuous skeletons.

3.2. Heat-treatment and crystallization

Fig. 4 shows the XRD patterns of BZ3 sample after heat-treatment at different temperatures. It is noted that the diffraction peaks are weak in as-dried sample and the one heat-treated in 800 °C, indicating low crystallinity. Because the precursor BaCl₂·2H₂O does not dissolve in EtOH liquid, the BaCl₂ concentration in the system nearly reaches its

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