



Synthesis of mesoporous $\text{La}_2\text{Zr}_2\text{O}_7$ with high surface area by combining epoxide-mediated sol-gel process and solvothermal treatment



Shengxue Wang, Wei Li*, Song Wang, Zhaohui Chen

Science and Technology on Advanced Ceramic Fibers and Composites Laboratory, National University of Defense Technology, Changsha 410073, China

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ABSTRACT

Mesoporous $\text{La}_2\text{Zr}_2\text{O}_7$ was successfully prepared by combining epoxide-mediated sol-gel process and solvothermal treatment. The gelation was controlled by addition of propylene oxide to the ethanol solutions of nitrates. Solvothermal treatment was adopted to strengthen the mesopore structure and inhibit the collapse of pores during ambient pressure drying, and it obviously increased surface area. The as-synthesized mesoporous $\text{La}_2\text{Zr}_2\text{O}_7$ showed nanoparticles assembling and mesoporous structure, and the nanoparticles have a surface area of $302.9 \text{ m}^2/\text{g}$ and an average pore size of 22.2 nm . The mesoporous $\text{La}_2\text{Zr}_2\text{O}_7$ has an amorphous structure with some organic component. After heat treatment, the inorganic transformation occurred and it crystallized into pyrochlore structure. With increase of heat treatment temperature, the particles of mesoporous $\text{La}_2\text{Zr}_2\text{O}_7$ become larger for the sintering of nanocrystalline $\text{La}_2\text{Zr}_2\text{O}_7$. The surface area can retain at $92.7 \text{ m}^2/\text{g}$ after 600°C , and decreased to $12.4 \text{ m}^2/\text{g}$ after 1200°C for 3 h. This facile route provides a low-cost strategy for the preparation of mesoporous metal oxide with high surface area.

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1. Introduction

Lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$, LZO) has attracted considerable attention because of its high melting point (2300°C), low thermal conductivity ($1.56 \text{ W m}^{-1} \text{ K}^{-1}$, 1000°C), excellent thermal stability, and high tolerance to defects [1–4]. It is well known that the high efficiency of mesoporous materials as physical adsorbents is due to their high pore volumes and large specific surface areas [5,6]. Mesoporous LZO with high surface area is expected to have important applications in the fields of catalysis, adsorption, energy conversion, sensing and fuel cells [7–13]. Especially, with excellent high-temperature stability and sintering resistance, mesoporous LZO is expected to serve as substitute for traditional Al_2O_3 as high-temperature catalyst carriers [14].

Presently, several synthesis methods have been utilized to prepare mesoporous LZO materials, e.g., hydrothermal synthesis, coprecipitation routes, combustion synthesis, molten salt method, and sol-gel method [15–18]. Of these methods, the sol-gel method can produce materials with high compositional homogeneity and

stoichiometry control [19,20], especially suitable for binary or multicomponent materials synthesis. Recently, an epoxide-mediated sol-gel process, which utilized organic epoxides as initiators for the sol-gel polymerization of simple inorganic metal salts, was developed by Gash et al. [21]. This method uses metal salts substituted for traditional alkoxides that are expensive and sensitive to moisture, heat and light [22]. Meanwhile, this process uses epoxide as proton consumer, which can increase the solution pH more moderately and uniformly than ammonia or urea. The epoxide-mediated sol-gel process is beneficial for the synthesis of many main groups, transition metal, and rare earth metal oxides with well-defined mesoporous microstructure. Some mesoporous oxides, such as silica [23–25], alumina [26], zirconia [27], $\text{ZrO}_2\text{--Y}_2\text{O}_3$ [28], mullites [29,30], $\text{SiO}_2\text{--TiO}_2$ [31], $\text{Y}_3\text{Al}_5\text{O}_{12}$ [32], and cordierite [33], have been successfully synthesized by the epoxide-mediated sol-gel process. However, the high surface area of mesoporous oxides are usually obtained by supercritical drying, which needs the use of expensive autoclaves to provide high pressures. This process restricts its industrial application due to production costs [34].

Solvothermal treatment is another effective way to obtain materials with high surface area, and can offer many advantages

* Corresponding author.

E-mail address: liwei3205@163.com (W. Li).

including the control of morphologies, pore size and phase transformation [35]. This process has been extensively utilized as a low-temperature processing to produce nanoscale materials in an organic medium at elevated pressures. Thus, one can obtain mesoporous LZO with high surface area by combining the epoxide-mediated sol-gel process and solvothermal treatment. For example, Inoue et al. [36] prepared nanocrystalline tetragonal ZrO_2 particles with diameter of 4–10 nm and surface area of 90–160 m^2/g . Konishi et al. [37] synthesized mesoporous ZrO_2 by combining alkoxy-derived sol-gel process and the solvothermal process, and the resultant macro-mesoporous crystalline ZrO_2 gels possess the surface area over 200 m^2/g .

In the present work, we demonstrate the synthesis of mesoporous LZO by combining epoxide-mediated sol-gel process and solvothermal treatment. Nitrates of La(III) and Zr(IV) has been used as precursors, which is adopt to synthesize mesoporous metal oxide in the presence of epoxide as gelation inducer. The as-prepared LZO has a uniform mesoporous structure, with no phase separation of La(III) and Zr(IV) compounds. In addition, the surface area of this materials is high and remains relatively stable after heat treatment. In addition, this synthetic strategy can be extended for the preparation of other multicomponent porous metal oxides.

2. Experimental

2.1. Synthesis

Zirconium nitrate pentahydrate (ZNO , $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$, Sinopharm Chemical Co., China, AR) and lanthanum nitrate hexahydrate (LNO , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Aladdin Co., China, AR) were chosen as starting materials, and ethanol was used as solvent. Propylene oxide (PO, Sinopharm Chemical Co., China, AR) was added to initiate gelation. For a typical synthesis, firstly, 3.000 g LNO and 3.024 g ZNO were dissolved in 50 mL EtOH under magnetic stirring at 60 °C. When turning clear, the mixture was cooled to room temperature (25 °C). Then PO was slowly added to the resultant homogeneous solution under vigorous stirring. The molar ratio of PO to LNO was 4. After 2 min, the formed transparent sol was poured into a poly (tetrafluoroethylene) (PTFE) tube and transferred to a stainless-steel autoclave for solvothermal treatment at 100 °C to 200 °C under an autogenous pressure. After 20 h, the autoclave was cooled down slowly to ambient temperature. The resultant wet gel was evaporation-dried at 60 °C for 24 h and 200 °C for 3 h to obtain the LZO xerogels. Some samples were calcined at elevated temperatures up to 1400 °C in air for 3 h with a heating rate of 5 °C/min.

2.2. Characterizations

The thermal behavior of LZO xerogels was examined from room temperature to 1400 °C using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis (STA49C, NETZSCH, Germany). The experiments were conducted in a flowing air atmosphere, with a heating rate of 10 K/min. X-ray diffraction (XRD) patterns were collected to analyze crystalline transformation on a Bruker Model D8 Advanced diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 30 mA and 40 kV. Data were recorded between 10° and 80°, with a step size of 4°/min. The corresponding interplanar distance (d) was calculated by the equation $\lambda = 2d\sin\theta$. The average crystal size (D) was calculated from the full width at half maximum (2ω) of the (622) diffraction peaks of the pyrochlore phase using Scherrer's equation [38–40]. Moreover, the morphology and microstructure of the materials were investigated using a scanning electron microscope (SEM, Quanta-200, EDAX Company) operating at 10 kV equipped with an energy dispersive X-ray spectrometer (EDS) and a transmission

electron microscopy (TEM, JEOL JEM2100) operating at 200 kV. Particle size distribution was analysed by a software Nano Measurer and the mean diameter of particles was calculated. Micro/mesopores were characterized by nitrogen adsorption–desorption isotherms using a Quantachrome instrument. The surface area was determined by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method using desorption branch. Before measurement, all the samples have been degassed at 200 °C at vacuum for 12 h.

3. Results and discussion

3.1. Effects of solvothermal treatment on microstructure of xerogels

Fig. 1a shows the synthesis process for mesoporous LZO via epoxide-mediated sol-gel process and solvothermal treatment. The starting solution was homogeneous and transparent. With the addition of PO, a monolithic, white, translucent gel formed (as inset of Fig. 2a). This transformation was accompanied by an exothermic reaction. The gelation took place after 10 min–30 min at ambient temperature, depending on the PO content. As known, gelation of metal salt solution is conducted via the hydration, hydrolysis, and condensation of metal cation in aqueous solutions [14,41,42], and reactions of $\text{Zr}^{4+}/\text{La}^{3+}$ binary system can be shown in Fig. 1b. These reactions are promoted by the pH of the solutions. PO is protonated by $[\text{M}(\text{H}_2\text{O})_n]^{z+}$ ($\text{M} = \text{La}, \text{Zr}$) and then an irreversible ring-opening reaction is produced by a nucleophilic anionic base (NO_3^- in the present case) which increases the pH of the system [43–45]. The increase in pH accelerates the condensation reaction and eventually induces the gelation. The skeleton of formed gels was composed of La–O- and Zr–O- clusters, and some hydroxyl group on the surface. Noteworthy, gels were formed with no addition of water in the synthesis, because water which is necessary for gelation can be released from the hydrated precursor salts. As reported before [26], M–OH ($\text{M} = \text{Zr}, \text{La}$) on the gel surface which exists in the aqueous solution will form well-built neck via chemical bonds between adjacent particles. Hence, solvent exchange with EtOH, which can make part of M–OH groups replaced by M–OC₂H₅ groups, is often needed. The particle growth via hard aggregation can be inhibited by the surface passivation due to the presence of M–OC₂H₅ groups, which is beneficial to formation of mesopores. This method with no water addition can also excuse the solvent exchange. Meanwhile, no addition of water reduced the phase separation of La–O- and Zr–O- clusters with different solubilities in water and EtOH, and made the condensation reaction slow and controllable.

We refer to the xerogels prepared without solvothermal treatment as X-0, while the xerogels solvothermal treated at 100 °C, 150 °C, 200 °C as X-S100, X-S150 and X-S200, respectively. Fig. 2 shows the photographs and SEM images of xerogels after solvothermal treatment at different temperature. It can be found that X-0 is yellow and translucent, X-S100 shows an orange and translucent appearance, and X-S150 and X-S200 shows brown and opaque appearance. All xerogels were fragile and easily to be grinded to powders. As the SEM pictures of the xerogels represents, all samples are constructed by nanoparticles. Fig. 3 shows the particle size distribution and mean diameter calculated by Nano Measurer. Particle size distribution of X-S100 and X-0 is in the range from 30 nm to 80 nm, and the mean diameter is 61.3 nm and 56.8 nm, respectively. While X-S150 and X-S200 shows obviously larger particle size, with mean diameter of 90.9 nm and 96.8 nm, respectively. On the other hand, compared to the xerogels solvothermal treated at 200 °C, X-S150 shows a more uniform color in appearance, and the particle size and shape is more uniform. As

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