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Gelcasting of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3\text{-}\delta}$ from oxide and carbonate powders

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Abstract

Perovskite ceramics have been successfully prepared by gelcasting from oxide and carbonate powders, which is characterized by sintering homogeneous gelcast obtained from a dense suspension of insoluble or low-solubility metal-oxide precursors and organic monomers. Especially, the porous perovskite ceramics can be obtained by controlling sintering process. Gelcasting of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3\text{-}\delta}$ was used to illustrate the process. The porosity, pore size, gas permeability and microstructure of the ceramics obtained were also characterized. This work shows that the obtained specimens are good enough for practical use and this preparation routine is very promising for preparing porous perovskite ceramics due to the specific advantages of simple processing.

Keywords: D. Perovskite; Porous ceramic; Preparation; Gelcasting

1. Introduction

Perovskite-type (ABO_3) oxides have been extensively studied for many technical applications such as in: catalysis [1], high temperature ceramic superconductors [2], and electronics. [3]. Furthermore, they are selected as electrodes for solid oxide fuel cells (SOFC) [4] and oxygen gas separation membranes [5] because of oxygen-sorptive and electronic conductive properties. Generally, perovskite ceramics have been fabricated from perovskite powders which are synthesized by conventional solid state reaction method as well as wet chemical processes including the thermal decomposition of cyanide [6], hydroxides, metal–EDTA [7] and oxalic complexes, chemical coprecipitation, sol–gel process [8]. It obviously makes the process simple that perovskite ceramics are directly prepared from metal oxide and its precursor powders, therefore gelcasting will be introduced to realize this aim in this work.

The gelcasting process, which has been developed since the 1990s, is based on a synthesis of ideas from both traditional ceramic processing and polymer chemistry, and the key part of the process is use of a monomer solution, which can be polymerized to form a strong, crosslinked polymer–solvent gel [9]. Although developed for the production of complex-shaped parts, gelcasting can be used to produce simple ceramic parts. The authors have introduced gelcasting to prepare porous α-$A1_2O_3$ ceramics [10] and to synthesize complex oxides. [11]

In this work perovskite $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3\text{-}\delta}$ ceramic with high oxygen ionic and electronic conductivity [5] was selected to illustrate this process, and the ceramics obtained were also characterized.

2. Experimental procedure

2.1. Samples preparation

Insoluble or low-solubility metal precursors are employed to form a dense suspension solidified by the polymerization of organic monomers after which the homogeneous gelcast is dried and then sintered at a temperature producing ceramics.

The starting materials (metal-oxide precursors) were lanthanum (La_2O_3), strontium carbonate ($SrCO_3$), basic cobalt carbonate ($2CoCO_3{\cdot}3Co(OH)_2{\cdot}xH_2O$) and iron oxide ($Fe_2O_3$). $2CoCO_3{\cdot}3Co(OH)_2{\cdot}xH_2O$ is very hygroscopic, and in this experiment the crystal water content x is 6.14 from thermogravimetric analysis. The chemicals, mixed in aqueous monomers (acrylamide, AM and

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N,*N*′-methylenebis-acrylamide, MBAM, AM:MBAM = 20:1(wt)) solution with a concentration of 10 wt% in stoichiometric ratio of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSC FO) were ball-milled. The resulting slurry with the initiator ammonium bisulphate $(NH_4)_2S_2O_8$ (1.6 wt% of organic monomers) was cast into a mold and solidified by heating at 45°C for 20 min. The dried gelcasts were machined and finished to discs of diameter 25×2 mm in size, which were then sintered in a programmable HT furnace (Nabertherm, Germany) under different conditions for later measurements.

3. Characterization

Simultaneous differential thermal analysis and thermogravimetry (DTA-TG) were carried out on the dried gelcasts obtained using a thermal analyzer (Netzsch STA 429). Samples were heated from 25 to 1300°C at a heating rate of $1°C\,min^{-1}$ under dynamic air flow. The gelcasts sintered in static air for 8 h from 800 to 1300°C were characterized by X-ray diffraction (XRD). The open porosity and total porosity of sintered specimens was obtained using the Archimedes method with a theoretical density for $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCFO) taken as $6.448\,g\,CM^{-3}$. Microstructure characterization of all specimens was carried out on a Hitachi X-650 Scanning Electronic Microscope (Japan). The bubble-point measurement was employed to get pore size distribution and the presence of defects, in the specimens, which is recognized as an ASTM procedure (F316-80 [12]and E128-61 [13]). Nitrogen gas permeation through resulting ceramic discs was measured in a home-made permeation device. This permeation device consisted of a permeation cell for holding the membrane sample, a pressure meter (for measuring upstream pressure), a differential pressure meter (for determining the transmembrane pressure difference) and a mass flow controller (for permeation flow rate). For a disc sample, the permeability data at various pressure differences were measured.

4. Results and discussion

4.1. DTA-TG

DTA-TG was used in analysing the thermal decomposition of the gelcasts and the formation of LSCFO perovskite phase. Fig. 1 shows the DTA-TG results of the gelcast in air. At $T < 240°C$, there is a ca. 9% mass loss which is caused by the endothermic removal of crystal water of $2CoCO_3{\cdot}3Co(OH)_2{\cdot}xH_2O$ and occluded water of the polymer network in gelcast specimens. In the temperature range 240–350°C, there is a mass loss for the specimen accompanied by a large exothermic DTA peak, this attributes to the bum-out of the cross-linked polymer network. At ca. 700°C, another mass loss starts which is complete at ca. 920°C. This is ascribed to the thermal decomposition of $SrCO_3$ and $2CoCO_3{\cdot}3Co(OH)_2$ due to solid-state reaction among carbonates and oxides and the formation of LSCFO perovskite phase, as evidenced by XRD. No apparent mass loss occurs at $T < 920°C$, indicating the decomposition of $SrCO_3$and $2CoCO_3{\cdot}3Co(OH)_2$ is complete.

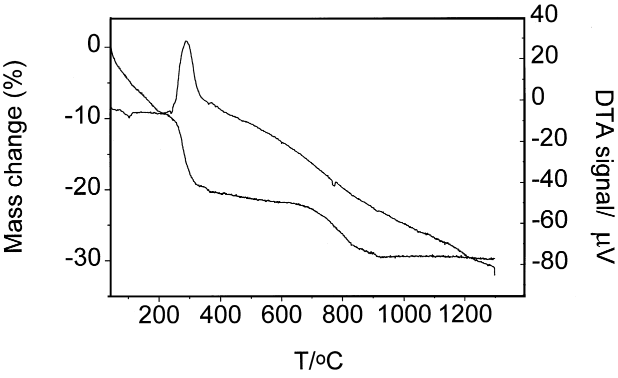

Fig. 1. DTA and TG curves of the gelcast.

4.2. X-ray diffraction

The LSCFO gelcasts were sintered between 800 and 1300°C, at 100°C intervals, for 8 h, and the products were identified by XRD. At 800°C, only carbonate and oxide were present and no perovskite phase were formed for specimens. When the temperature was raised to 900°C, the solid-state reaction lead to the formation of perovskite phase with a corresponding decrease in carbonate and oxide phases. Most of the oxides in LSCFO products were changed to perovskite phase at 1000 °C, and until 1100°C perovskite-type LSCFO was formed completely. When the firing temperature was further raised to 1300°C, the specimens retained the perovskite phase. All perovskite-type specimens exhibited a metallic lustre to some extent. XRD pattern of typical perovskite phase from LSCFO gelcast is shown in Fig. 2. These indicate that pure perovskite phase can be obtained at lower temperature as compared to the conventional solid-state reaction method.

4.3. Porosity, pore size distribution and linear sintered shrinkage

Fig. 3 shows the open porosity vs sintering temperature for the specimen. At 1100°C, the total and open porosity of the specimen is 48.9 and 48.3%, respectively, in which pure perovskite phase just formed. When the temperature is raised to 1350°C, the total and open porosity of specimens decreases up to 13.1 and 1.3%, respectively, while the closed porosity rises. It is possible that dense specimens can be obtained by improving sintering process. In addition, when sintering temperature is chosen, the open porosity of specimens is large enough to be used as porous ceramic substrates, because it has been found that an asymmetric configuration is ideal for separation membrane with high flux [14] in which one or more separation layer is prepared on the surface of porous ceramic support. Perovskite porous ceramics are selected as the substrates of the perovskite layers, and this may avoid the interface action between two different materials. Also the pore size and pore size distribution of porous ceramics should be considered for their use. Fig. 4 shows the relationship between the mean pore size of specimen and sintering temperature. Their mean pore size changes from 0.90 to 0.71 μm in the temperature ranges of 1100–1250°C. Fig. 5 shows relatively narrow pore size distribution for specimens. It should also be noted that the maximum pore size in specimens is lower than 2.3 μm indicating no flaws and cracks existed in the specimens. The linear shrinkage of specimen sintered at 1350°C for 8 h is 28.5%, and therefore it is not difficult for sintering process to be controlled.

4.4. Microstructure development

SEM photographs of fracture surface of the dried gelcasts, sintered gelcasts at 1100, 1250 and 1350°C for 8 h are shown in Fig. 6(a)–(d). From Fig. 6(a), it can be seen that the dried gelcasts have homogeneous small particles of submicrometer size kept together by the crosslinked polymer. Such highly reactive small particles are ideal for the consequent solid-state reaction and sintering to form porous perovskite ceramics. Fig. 6(b) and Fig. 6(c) show the reaction takes place and leads to grain growth for the specimen, and formed perovskite grains grow from *ca.* 1 μm at 1100°C to *ca.* 2 μm at 1250°C. Up to 1350°C, the open pores nearly disappeared while closed pores decrease significantly. It can be also found that sintered specimens exhibit a well-defined morphology in the packing and sintering of particles which may provide high mechanical strength.

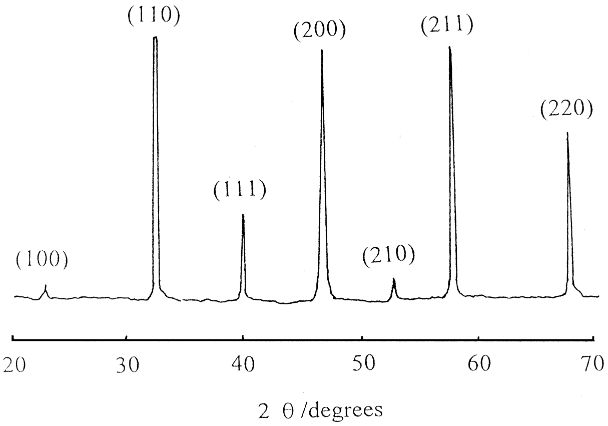

Fig. 2. X-ray diffraction pattern of perovskite phase produced by the specimen sintered at 1200°C for 8 h.

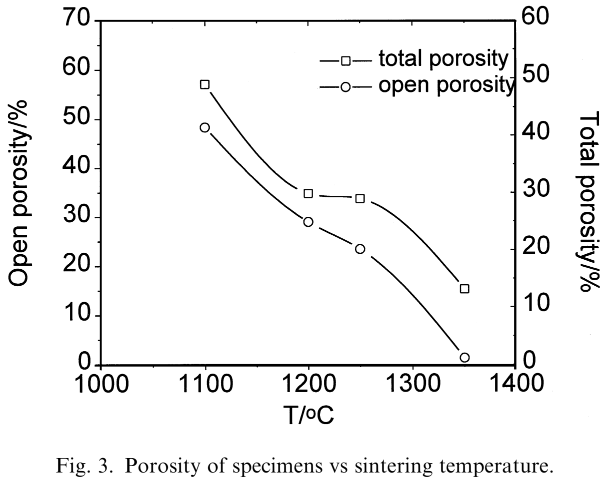

Fig. 3. Porosity of specimens vs sintering temperature.

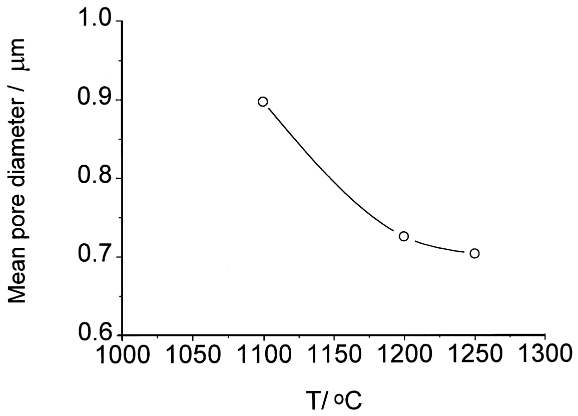

Fig. 4. Mean pore diameter of specimens vs sintering temperature.

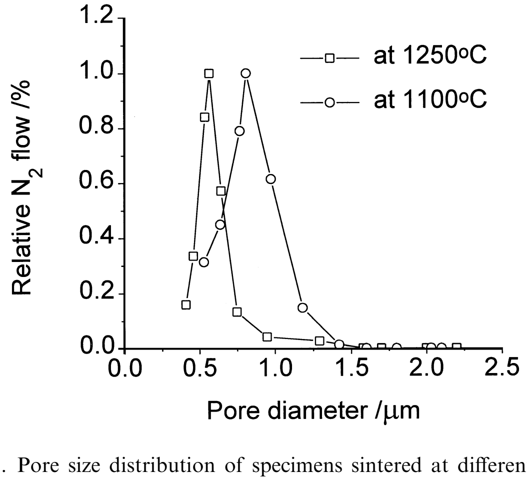

Fig. 5. Pore size distribution of specimens sintered at different temperature.

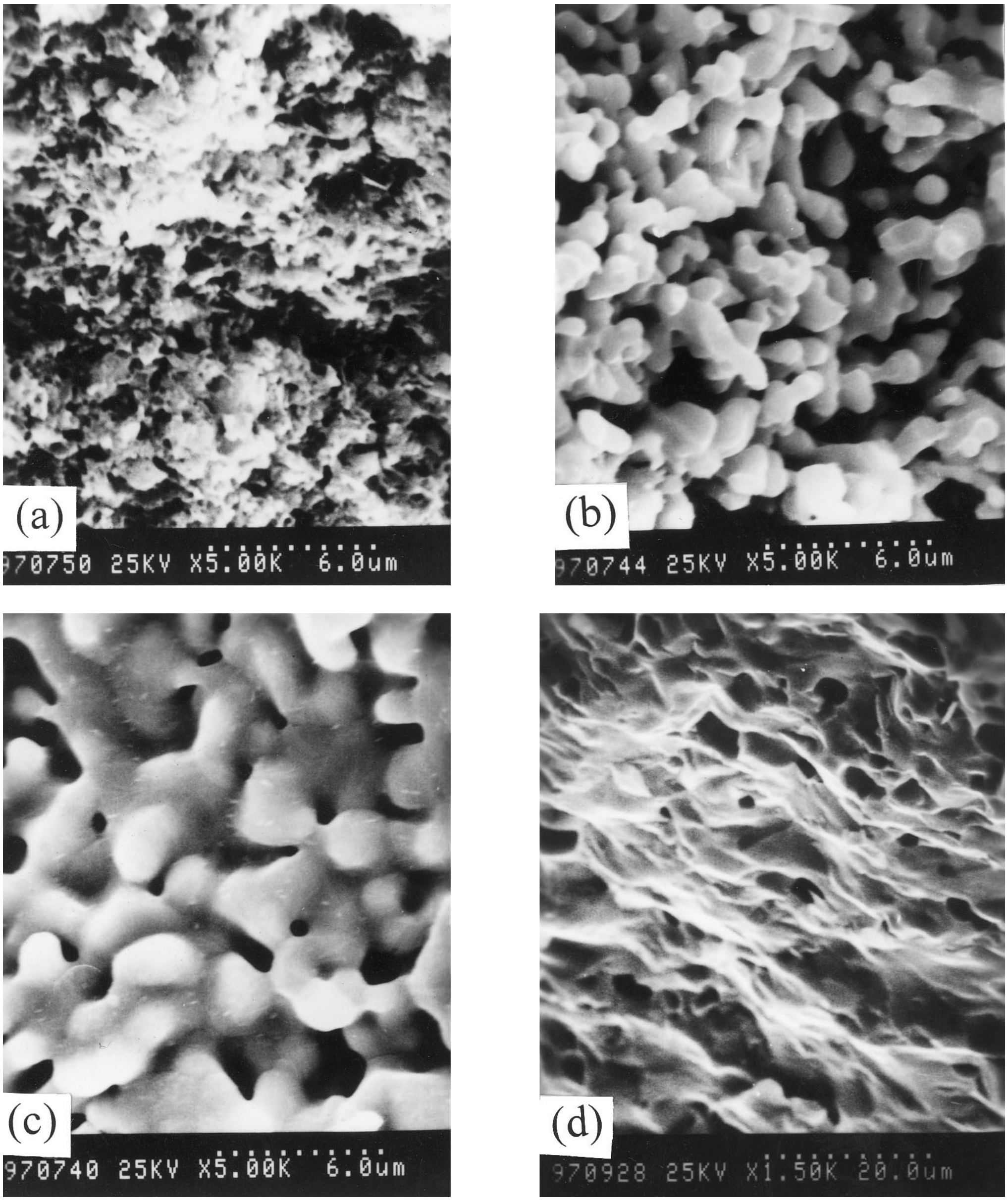

Fig. 6. Scanning electron micrographs of the dried gelcast (a) and specimens sintered at 1 100°C (b), 1250°C (c), and 1350°C for 8 h.

4.5. Permeability to nitrogen gas

The fluid flux of porous ceramics is commonly considered from the viewpoint of applications. Fig. 7 shows the result of gas permeation through the disc specimens sintered at 1100 and 1250°C for 8 h. As expected, the nitrogen flux increases linearly with pressure drop across disc specimens. The nitrogen permeability of the specimens is 8.83×10^2–$1.46\times10^2\,\mathrm{m^3\,m^2}$ bar h, respectively, which is accordance with symmetric membrane with the same porosity and pore size, but lower than that of asymmetric microfiltration membranes [15].

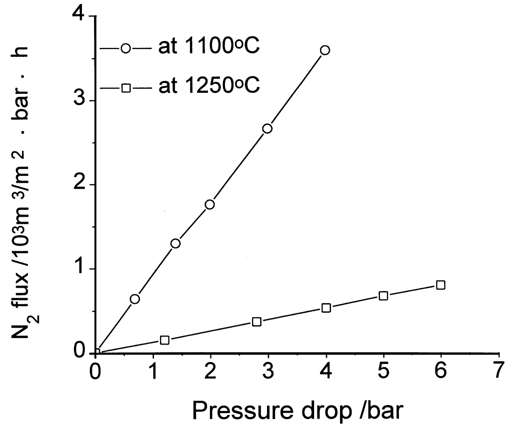

Fig. 7. Nitrogen flux of specimens sintered at different temperature.

5. Conclusion

1. Perovskite ceramics have been successfully prepared by gelcasting using oxide and carbonate powders, and practical porous perovskite ceramics can be obtained by controlling the sintering process. This method has the specific advantages of simple processing, homogenous solid-state reaction and sintering process in one step, and hence it is an promising method for preparing porous perovskite ceramics for practical use.
2. As an example, porous perovskite-type $La_{0.6}Sr_{0.4}$-$Co_{0.8}Fe_{0.2}O_{3-\delta}$ was prepared from oxide and carbonate powders. The study indicates that the porous ceramics obtained have homogenous grain size and pore size. The open porosity and mean pore size of porous ceramics sintered at 1100–1250°C for 8 h are in the ranges of 48.3–23.5% and 0.90 μm–0.71 μm, respectively. The nitrogen permeability are correspondingly in the range of 8.83×10^2–$1.46\times10^2 m^3 m^2$ bar h. These mean that the specimens are good enough for the use as supports for other inorganic membrane fabrication. Dense perovskite ceramics should be obtained as sintering process is adequately controlled.

Acknowledgements

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