

Preparation of calcium doped LaCrO_3 fine powders by hydrothermal method and its sintering

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Abstract

The synthesis of fine powders of LaCrO_3 and its solid solutions doped with calcium under hydrothermal conditions and the sintering of these powders were investigated. Precursor alkaline coprecipitated lanthanum chromite gels with three different compositions: LaCrO_3 , $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$, were processed under hydrothermal conditions at low temperatures (350–425 °C), for a reaction time between 30 and 120 min. Powders of a single phase with orthorhombic structure of LaCrO_3 , $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$ were obtained at a temperature as low as 350, 400 and 425 °C, respectively, for a short reaction interval of 1 h. SEM and TEM micrographs showed that particles with an irregular morphology and an average particle size of 300 nm, were mainly obtained under hydrothermal conditions. The powders were pressed by cold isostatic pressing at 200 MPa, and then sintered in air at a temperature range of 1200–1500 °C for various intervals (1 to 5 h). A maximum apparent density of 97.7% was achieved on specimens with high calcium content, $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$, at 1400 °C for 5 h. The average grain size measured on the sintered specimens was 6 μm.

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1. Introduction

Lanthanum chromite powders substituted with alkaline metals (Ca or Sr) have been widely accepted as the candidate for interconnection materials in the present generation of Solid Oxide Fuel Cells (SOFCs).¹ The interconnector in SOFCs must be stable under reducing and oxidizing atmospheres, and must possess an adequate electronic conductivity in both atmospheres, as well as, thermochemical compatibility with other cell components under operating conditions^{1,2} and have high density (typically >94% of the theoretical).³

It has been found that a partial substitution of lanthanum ions with an alkaline metal ions, such as: Ca or Sr, is likely to increase chemical stability and electric conductivity of pure lanthanum chromite.⁴ Recently, various chemical routes

have been used to process lanthanum chromite powders such as glycine nitrate process,⁵ oxalic salt method,⁶ hydrazine,⁷ coprecipitation⁸ and sol-gel.⁹ These chemical processes, however, involve a heat treatment which is normally conducted at temperatures between 700 and 800 °C, in order to obtain the crystalline phase. Furthermore, a milling stage is required in order to disperse the agglomerated particles formed during the heat treatment.

On the other hand, the sintering of LaCrO_3 powders assisted by the presence of a liquid phase has been the main focus of investigation. It was found that the incorporation of $\text{Ca}(\text{CrO}_4)$ particles allows the sintering to proceed at temperatures between 1300 and 1500 °C in air, because this compound forms a transient liquid phase at above 1076 °C.¹⁰ High dense Ca-doped lanthanum chromite specimens with a relative density of 97% of the theoretical value, were obtained by heat treatments in air at 1550 °C for 20 h. However, the sintering is also difficult due to a significant

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volatilization of chromium oxide at high temperatures in oxidizing atmosphere.¹

Hitherto, it was found that sinterability of LaCrO_3 and its solid solution doped with Ca might be achieved by several factors of the raw powder, such as: high purity, controlled particle morphology, and nanometric particle size.¹¹ Thus, among the conventional or other non-conventional chemical synthesis processes, the hydrothermal technique is considered as a single step process that allows the synthesis of a wide variety of raw oxide powders, which fit more of the particular characteristics mentioned above.¹² Indeed, the first evidence of the synthesis of the LaCrO_3 pure compound under hydrothermal conditions was reported by Yoshimura et al.¹³ They prepared LaCrO_3 powders with a grain size of 0.7 μm , at 700 °C with a confining pressure of 100 MPa, the crystallization process of the stable perovskite phase was conducted in a platinum capsule by dissolving stoichiometric amount of the compounds $\text{La}(\text{OH})_3$ and Cr_2O_3 . In contrast, pure LaCrO_3 powders were prepared by the same ordinary hydrothermal treatment at lower temperature (260 °C). The powders were synthesized from La_2O_3 powder and CrCl_3 dissolved in an alkaline solution of KOH (8.5 M).¹⁴ The particles obtained under these conditions, had a cubic morphology with an average particle size of 3 μm . Although the crystallization of the single LaCrO_3 have been widely investigated by the hydrothermal method, neither the crystallization of alkaline metal doped lanthanum chromite under hydrothermal conditions nor its sintering have been investigated as yet. Therefore, we aimed to study the synthesis of pure lanthanum chromite (LaCrO_3) and its solid solution doped with calcium ($\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$) under hydrothermal conditions by employing a coprecipitated gel containing the raw constituents (La and Cr) and the dopant element (Ca), at lower temperatures (300–425 °C). In addition, the sintering of the powders obtained during the hydrothermal treatments was studied by conventional heat treatment in air. The differences on the microstructure of the specimens sintered under these conditions are discussed on base of the size and the morphology of the hydrothermally synthesized powders. The sinterability of these powders was compared with that reported in the former literature for doped lanthanum chromite powders prepared by different chemical methods.

2. Experimental

2.1. Hydrothermal synthesis

Precursor lanthanum chromite gel was prepared by the alkaline coprecipitation method reported by Inagaki et al.,¹⁵ employing reagent grade chemicals of: $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (99.9%), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99.9%), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (99%) and NaOH (99.998%) (Wako Pure Chemical Industries, Ltd., Japan). Aqueous solutions with a concentration 0.05 M of LaCl_3 , $\text{Cr}(\text{NO}_3)_3$ and CaCl_2 were prepared with deionized water, and a solution of 0.5 M of NaOH was employed as coprecip-

itation media. In a typical procedure, a volume of 475 ml of the precipitating solution (NaOH) was poured in a biker, and the solution of chromium (500 ml) was then mixed, which results in the formation of an opaque whitish green precipitate. The vigorous stirring of the mixed solutions leads to the dissolution of the preliminary precipitated gel of $\text{Cr}(\text{OH})_3$. Finally, the coprecipitation of the complex gel was carried out by the addition of the same volume (500 ml) of the solution containing the other elements, La or the mixture of La + Ca. The solutions were mixed in three different volumetric ratios, La:Ca:Cr, 1:0:1, 0.9:0.1:1 and 0.8:0.2:1; which matches the compositional stoichiometric of the solid solutions, LaCrO_3 , $\text{La}_{0.9}\text{Ca}_{0.1}\text{CrO}_3$ and $\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$. The coprecipitated gel was centrifuged and a volume of 20 ml was then poured into a hydrothermal Hastelloy C-lined microautoclave (40 ml capacity). The vessel was heated at a constant rate of 20 °C/min up at various temperatures (350–425 °C) for a reaction interval between 0.5 and 2 h. After the treatments, the precipitates were well washed with distilled water, decanted and then dried in an oven at 100 °C overnight.

2.2. Sintering

The sintering of the powders was conducted by a conventional firing in air. The powders (0.5 g) were poured into a tungsten carbide die (10 mm diameter) and pressed by hand, the formed pellets were then cold isostatic pressed at 200 MPa for 5 min. The green compacts were heated at a constant heating rate of 10 °C/min up to the desired temperature. The sintering was conducted in air at a temperature range between 1200 and 1500 °C for several reaction intervals from 1 to 5 h.

2.3. Characterization

Powder X-ray diffraction analyses were carried out to determine the crystalline phases and the lattice parameter constants of the synthesized powder. Measurements were made by an X-ray diffractometer (Rigaku Rotaflex) with graphite-monochromatized $\text{Cu K}\alpha$ radiation at 40 kV and 100 mA. Diffraction patterns were taken from 10 to 70° at a scanning speed of 4°/min. The lattice parameters were calculated by the least square method from the diffraction peaks collected in the 2θ range from 20 to 60° at a scanning speed of 0.4°/min and step sampling interval of 0.006°, using Si as an internal standard. The theoretical densities of the hydrothermally synthesized powders were calculated from the lattice parameters data. Moreover, morphological aspects of the powders were examined by scanning electron microscopy (SEM, Philips XL30 ESEM) equipped with an energy dispersive X-ray (EDX) analyzer. In addition, the particle size was measured by transmission electron microscopy (TEM, Phillips CM200).

In addition, the sintered specimens were polished to mirror like surface, followed by a thermal etching, which was conducted at 1020 to 1275 °C for 2 h in order to reveal the microstructure. The apparent density of the sintered

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