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LETTER

Effect of CaF_2 on the sintering and thermal expansion of $La_{0.85}Sr_{0.15}Cr_{0.95}O_3$

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Lanthanum chromite based perovskite have been widely accepted as ceramic interconnects and as protecting layers for metallic interconnects in solid oxide fuel cells (SOFCs) because of thier high electronic conductivity, chemical stability in both oxidizing and reducing atmospheres as well as their chemical and thermo-mechanical compatibility with other cell components under operating conditions [1, 2]. Strontium-doped $LaCrO_3$ has emerged as a primary candidate for SOFC interconnects over other alkaline earth oxides such as CaO and MgO [3]. From the viewpoint of compatibility of thermal expansion among SOFC components, Sr-doped lanthanum chromite can match the coefficient of thermal expansion (CTE) to the Y_2O_3-stabilized ZrO_2 (YSZ) electrolyte using less than 20 mol% Sr [4].

Lanthanum chromite interconnects must be a dense in order to separate fuel gas from the oxidizing agent. They are usually sintered above 1,600 °C to reach a 94% relative density [5]. From cost considerations associated with commercialization, it is desirable for all components of SOFCs to be co-sintered in air to reduce manufacturing costs. However, this may cause severe reactions among the components at high temperature. Therefore, lowering the sintering temperature of the $LaCrO_3$-based interconnect is favored. However, the volatilization of CrO_3 in $LaCrO_3$ at high temperature in air makes it difficult to sinter. Some researchers have attempted to improve the sinterability of $LaCrO_3$ powders in different ways. Sakai et al. [6] found that chromium deficient lanthanum calcium chromites ($La_{0.7}Ca_{0.3}Cr_{1-y}O_3$, $y = 0.02$) could be sintered to 94% theoretical density at 1,200 °C in air. Small particle sizes of the starting powders prepared by chemical process are usually beneficial to lower the sintering temperature [7]. Doping with sintering additives is another effective method to densify $LaCrO_3$. A small amount of $Sr_3(VO_4)_2$ [8] was found to produce high density $LaCrO_3$-based perovskite materials sintered at 1,550 °C in air. Alternatively, low melting point eutectics, such as LaF_3, YF_3 and MgF_2, up to 8–10 wt% were added to densify $LaCrO_3$ at 1,400 °C in air [9].

The aim of the work described here is to experimentally investigate the sintering and thermal expansion behaviors of $La_{0.85}Sr_{0.15}Cr_{0.95}O_3$ (LSC) ceramics by using calcium fluoride as an additive.

Strontium-doped lanthanum chromite powders were synthesized using traditional ceramic processing methods. The starting powders La_2O_3, $SrCO_3$, Cr_2O_3 (>99.9 wt%) were mixed with distilled water using ZrO_2 milling media in a ball mill. After drying, the powders were calcined at 1,000 °C prior to adding the sintering additive. Then various amounts of CaF_2 (0–0.9 wt%) were added to the calcined powders. The mixed powders were milled again and dried. After granulitization, the powders were pressed into pellets 20 mm in diameter and 2 mm in thickness under a pressure of 72 MPa. The green bodies were then sintered at selected temperatures with a heating rate of 2 °C/min in air and a holding time of 3 h.

The particle size distribution of the calcined powders was measured using a particle-size analyzer (NSKC-A, Nanjing University of Technology, Nanjing, China). The bulk densities of the sintered pellets were measured by Archimedes method with de-ionized water. The crystal structure of the sintered samples was analyzed using X-ray diffraction (XRD, D/max-β, Rigaku) with CuKα radiation in the

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2θrange 18–80°. The microstructures of sintered samples (phosphoric acid etched well-polished surfaces) were observed using scanning electron microscopy (SEM, Model Jsm-5900, JEP, Tokyo, Japan). Thermal expansion measurements were conducted on sintered bars (~52 × 5 × 5 mm) using a high temperature dilatometer (RPZ-01, Luoyang Institute of Refractories Research, Luoyang, China) with a heating rate of 5 °C/min from room temperature to 1,000 °C in air or in a reducing atmosphere.

Figure 1 shows the particle size distribution of the LSC power milled for 8 h after being calcined at 1,000 °C. The value of the medium diameter is 0.46 μm, i.e. a considerable small particle size favorable to sintering. The result is similar for all CaF_2-doped LSC powder.

Figure 2 shows the bulk density of LSC as a function of CaF_2 content. The densities of all samples increase with sintering temperature. It also can be seen that the bulk densities of the samples sintered at 1,400 °C are very close to those sintered at 1,450 °C, which indicates that too high a sintering temperature seems unfavorable in terms of the densification of CaF_2-doped LSC ceramics in the current system. As for the samples sintered at 1,400 °C, when the CaF_2 addition reaches 0.7 wt%, the bulk density shows a marked increase from 5.79 g/cm^3 to 6.19 g/cm^3, which is 94.9% of the theory density, while an opposite tendency can be seen for those sintered at 1,350 °C.

Sakai et al. have reported that the poor sinterability of $LaCrO_3$ could be ascribed to the formation of a thin layer of Cr_2O_3 forming from the vaporization of CrO_3 at the interparticle neck during the initial stage of sintering in air [2]. They also indicated that a B-site deficit could suppress chromium vaporization from the particles, lowering the sintering temperature and enhance the sintering by inhibiting the formation of Cr_2O_3 [6]. Flandermeyer et al. [9] have found that some fluoride (LaF_3, YF_3, etc.) as well as oxide eutectics (CaO, NiO, etc.) are quite effective in completing densification of $La(Cr,Mg)O_3$ perovskite at 1,673 K in air. For the present study, as CaF_2 increases, it may form a liquid phase and prevent the forming of thin layer of Cr_2O_3, thus it improved the sinterability of LSC ceramics.

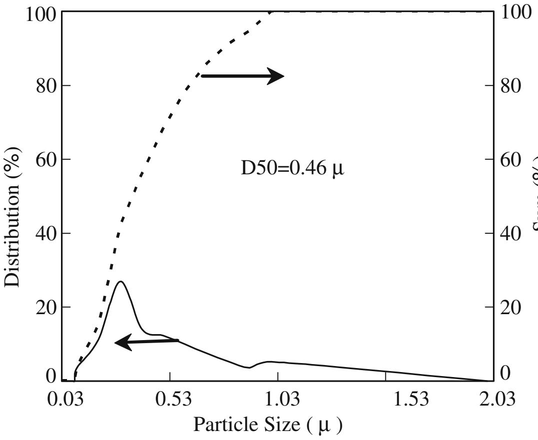

Fig. 1 Particle size distribution of a LSC powder milled for 8 h after being calcined at 1,000 °C for 2 h in air

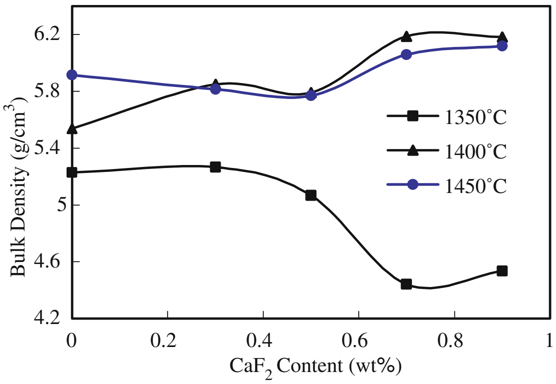

Fig. 2 Bulk density of LSC samples sintered at 1,350, 1,400 and 1,450 °C with holding time of 3 h as a function of various CaF_2 contents

Figure 3 shows the XRD patterns of 0.7 wt%-CaF_2-doped LSC samples sintered at 1,350, 1,400 and 1,450 °C. All the samples show only the pure perovskite phase with orthorhombic symmetry and no other phases were observed. This indicates that the foreign Ca^{2+} ions have entered the $LaCrO_3$ perovskite crystal lattice. The lattice parameters and crystal symmetries of 0.7 wt%-CaF_2-doped LSC samples sintered at 1,350, 1,400 and 1,450 °C are summarized in Table 1. The data are similar to those reported by many authors [3, 10]. It was found that the samples sintered at higher sintering temperatures showed smaller lattice parameters compared with those with lower

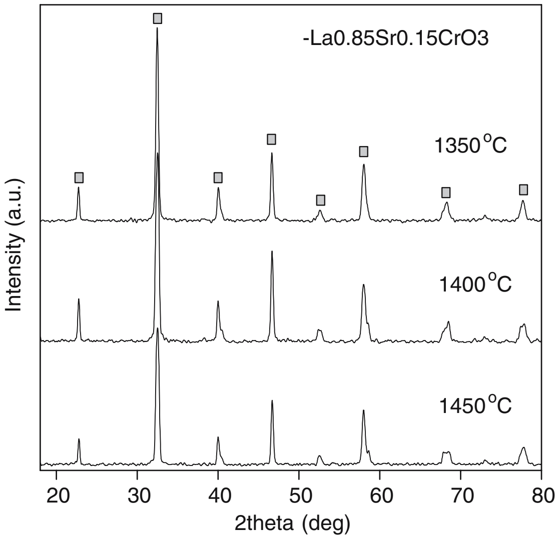

Fig. 3 XRD pattern of 0.7 wt%-CaF_2-doped LSC sintered at 1,350, 1,400, 1,450 °C for 3 h

Table 1 Crystal system, lattice parameters and cell volumes of 0.7 wt%-CaF_2-doped-LSC samples

Sintering temperature (°C)	Crystal system	Lattice Parameters			Cell volume (×10^3 nm^3)
		a (nm)	b (nm)	c (nm)	
1,350	Orthorhombic	0.5485	0.5503	0.7793	235.22
1,400	Orthorhombic	0.5463	0.5495	0.7730	232.05
1,450	Orthorhombic	0.5453	0.5488	0.7749	231.90

firing temperatures. This result is consisted with the work of Mori et al. [11]. It is believed that with the increase of sintering temperature, the Ca has reacted with $LaCrO_3$ particles and diffused into the $LaCrO_3$ perovskite [11]. The ionic radius of Ca^{2+} (0.106 nm) is smaller than that of La^{3+} (0.122 nm), which caused a small decrease of cell volume when more Ca^{2+} replaced La^{3+} with the increasing of sintering temperature.

Figure 4 shows the SEM images of a polished and acid etched surface of 0.7 wt%-CaF_2-doped LSC sintered at 1,350 and 1,400 °C. The grains of the sample sintered at 1,400 °C are strikingly larger than those sintered at 1,350 °C. In Fig. 4b, the grains are relatively close and uniform, and grain boundaries are clearly visible. While for the sample sintered at 1,350 °C as shown in Fig. 4a, the grain structure is less compact and many pores were observed among the grains. This result is in accordance with the density data exhibited in Fig. 2.

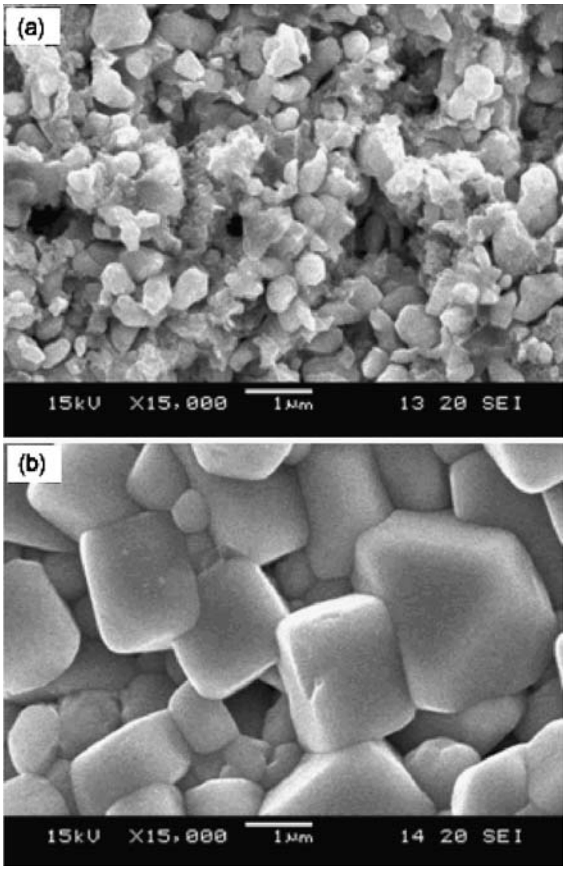

Fig. 4 SEM images of LSC doped with 0.7-wt%-CaF_2-doped LSC sintered at (a) 1,350 °C, (b) 1,400 °C

8YSZ (8 mol%-Y_2O_3-stabilized-ZrO_2) is the most common electrolyte in SOFCs, and the CTE of 8YSZ is ~10.3×10^{-6} °C^{-1} in the temperature range from 50 to 1,000 °C in air or a H_2 atmosphere [9]. Therefore, the $LaCrO_3$-based interconnect should a CTE which is approximately equal to that of 8YSZ.

Figure 5 shows the CTEs (50–1,000 °C) in air of LSC with various amounts of CaF_2 doping. The CTEs of the all samples are very close to that of 8YSZ electrolyte (as represented by the broken line in Fig. 5). Thus small amounts of CaF_2 doping have little impact on the CTEs of LSC perovskite.

Figure 6 shows the CTEs of 0.7 wt%-CaF_2-doped LSC perovskites in air and in a reducing atmosphere. The CTEs increase with temperature from 200 to 950 °C. The CTEs tend to increase with temperature because of volume expansion basically caused by the formation of point defects in the perovskites structure [12]. The CTEs of LSC in a reducing atmosphere are higher than in air. It was recognized that the lattice expansion of doped lanthanum chromite in reducing environments was related to the increase of oxygen vacancies, thus a coulomb repulsion between adjacent Cr cations occurred [12]. Another possible mechanism may be the size increase of chromium cations during reduction (as for the ionic radii, Cr^{4+} = 0.069 nm, Cr^{3+} = 0.0755 nm) [13].

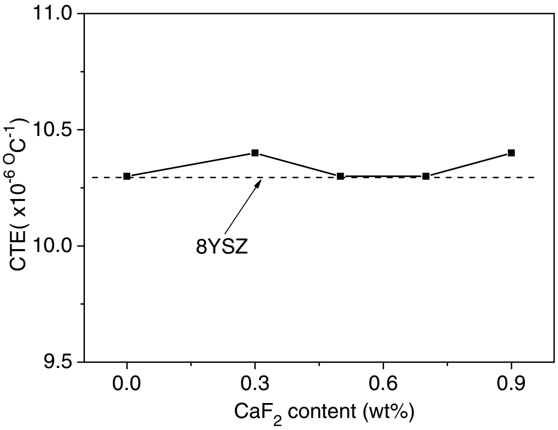

Fig. 5 CTEs of LSC as a function of CaF_2 dopant content in temperature range from 50 to 1,000 °C in air

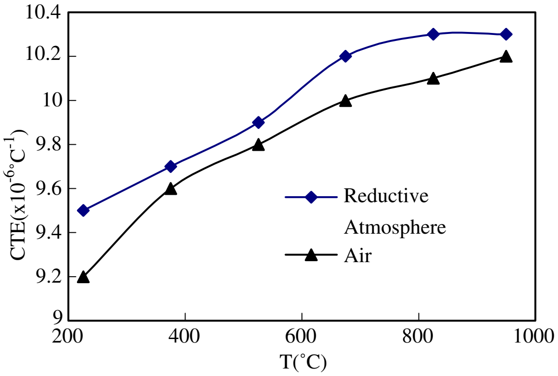

Fig. 6 CTEs of 0.7-wt%-CaF_2-doped LSC perovskite as a function of temperature in air and in a reducing atmosphere

In conclusion, the bulk density of LSC increases with CaF_2 content and sintering temperature. The LSC ceramics doped with 0.7 wt% CaF_2 and sintered at 1,400 °C reach 94.9% theoretical density. All 0.7 wt%-CaF_2-doped samples are pure perovskite phase with orthorhombic symmetry. The grains of the samples sintered at 1,400 °C are strikingly larger than those sintered at 1,350 °C. The CTE varies slightly with CaF_2 content. The average CTE of 0.7 wt%-CaF_2-doped LSC ceramic is 10.3×10^{-6} °C^{-1}, which is compatible with that of 8YSZ electrolyte. The CTEs of CaF_2-doped LSC ceramics show larger values in a reducing atmosphere than in air probably due to the increase in oxygen vacancies in a reducing atmosphere.

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