Two-Step Sintering of Samaria-Doped Ceria

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Abstract. Samaria-doped ceria is a candidate solid electrolyte for applications in intermediate-temperature solid oxide fuel cells. One of the main concerns related to this solid electrolyte is its low sinterability, even when prepared by chemical methods. In this work, an alternative method of sintering was used aiming obtaining high densification with negligible grain growth in the late stage of sintering. Commercial samaria-doped ceria powder was pressed into pellets and sintered following the two-step sintering process. The first (peak) temperature was varied from 1100 to 1500 ºC and the dwell temperature between 1050 and 1400 ºC with soaking time of 5 h. The sintered ceramics were characterized by several techniques to correlate the processing-property characteristics. Relatively high densification has been obtained. Electrical conductivity data obtained by impedance spectroscopy could account for the observed improved densification.

Introduction

Samaria-doped ceria (SDC) has received considerable attention due to its high ionic conductivity compared to the conventional yttria-stabilized zirconia solid electrolyte [1,2]. The reduction of the operation temperature of a Solid Oxide Fuel Cell (SOFC) by using a solid electrolyte with higher electrical conductivity than that of yttria-stabilized zirconia has been one of the main research goals, because it would reduce the overall cost of this type of device [2].

Samaria-doped ceria is one of the preferred candidates for solid electrolyte in SOFC. One of the main problems associated to ceria-based solid electrolytes is their relatively low sinterability, even when prepared from chemically synthesized powders [3]. The main approaches to overcome this problem are the use of a sintering aid or the use of a non-conventional sintering method, like fast firing. Recently, a new sintering process was reported by Chen and Wang [4]. The so-called two-step sintering was proposed aiming to produce ceramic materials with high densification and low grain size.

In the two-step sintering process the green compact is first conducted to a relatively high temperature (peak temperature), and after a short soaking time, the compact is fast cooled down to a given temperature (isothermal temperature) for a large holding time. The two-step sintering method exploits the competition between the driving forces of grain boundary controlled densification and grain boundary controlled grain growth to achieve densification without grain growth in the final stage of sintering [4,5]. It was shown in previous works that a specific density should be reached in the first step of sintering. For materials that densify by solid state reactions this minimum relative density is around 75% [6-8].

In this work, commercial samaria-doped ceria compacts were sintered following the two-step sintering process. The main purpose is to verify the feasibility of densification without grain growth in the late stage of sintering, and the effect of the sintering profile in the electrical conductivity.

Experimental

Commercial samaria-doped ceria, SDC1 ($Ce_{0.8}Sm_{0.2}O_{1.9}$, Fuel Cell Materials) was used as starting material. Green compacts were prepared by uniaxial followed by isostatic pressing. For comparison purposes, cerium oxide (CeO_2, 99.9%, Aldrich) and samarium oxide (Sm_2O_3, 99.9%, Aldrich) were used to prepare $Ce_{0.8}Sm_{0.2}O_{1.9}$ by the solid state synthesis method, hereafter called SDC2. In this case, the starting oxides were mixed together in the stoichiometric proportion in a mechanical mixer (Turbula, T2C) for 5 h in alcoholic medium and using zirconia balls. After drying, the mixture was deagglomerated in the mechanical mixer for 1 h. Cylindrical compacts were prepared using the same procedures as that for the commercial powder. Sintered pellets were obtained by varying the peak temperature and the isothermal temperature. The overall process was accomplished by heating up to the peak temperature and immediately cooling down to the isothermal temperature. The heating rates used up to the peak temperature were 2 ºC.min^{-1} and 10 ºC.min^{-1} for compacts prepared with the commercial powder and by the mixture of starting oxides, respectively. The cooling rate was 10ºC.min^{-1}.

The sintered density was determined by sample mass and geometry (bulk density). Phase characterization was accomplished by X-ray diffraction (D8 Advance, Bruker-AXS) using a Ni filtered Cu K$_\alpha$ radiation in the 20-80º 2θ range. Morphology of samples was observed by scanning electron microscopy (SEM, LEO Stereoscan 440) using secondary electrons. The average grain size of sintered pellets was estimated by the intercept method [9]. Electrical conductivity measurements were carried out by impedance spectroscopy using a low-frequency impedance analyzer (4192A, HP) in the 5 Hz to 13 MHz frequency range. Silver paste was applied by painting onto large surfaces of pellets to act as electrode material.

Results and discussion

Fig. 1 shows the evolution of the relative density with the peak temperature for SDC1 and SDC2 specimens.
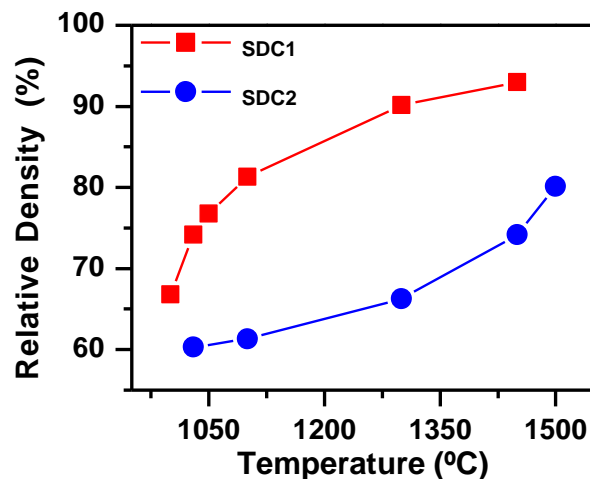

Fig. 1: Evolution of the sintered density with the peak temperature for SDC1 and SDC2 specimens.

The relative density increases gradually with the peak temperature for both types of samples. However, the relative density of the specimens prepared with commercial powder is at any temperature higher than that of the solid solution prepared from solid state reactions. For the peak temperature of 1500ºC the relative densities amount 93% (commercial powder) and 81% (obtained by solid state reactions). This result would be expected once it was shown that the solid solution formation in samaria-doped ceria requires a relatively high temperature for completion [10]. Then, most of the energy supplied to the system is consumed for solid solution formation up to about 1450ºC. This also explains the different behavior of the densification curves (Fig. 1).

Fig. 2 shows the relative density of SDC2 specimens after several dwell temperatures for a peak temperature of 1450ºC. The relative density shows a distinct behavior consisting of a low densification rate up to ~1300 ºC, and a fast densification for higher temperatures.
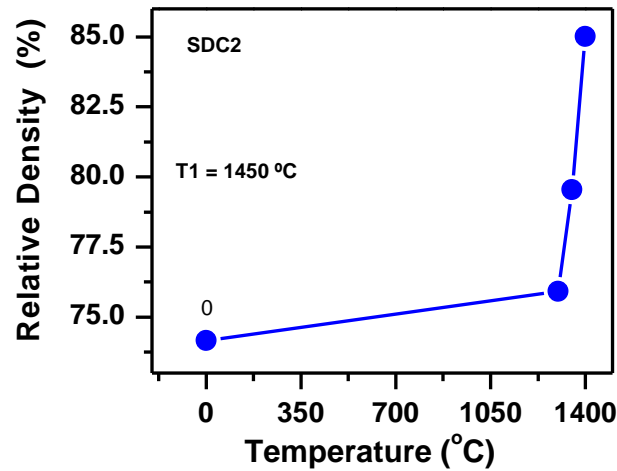

Fig. 2: Evolution of the sintered density with the dwell temperature for SDC2 specimens. Peak temperature = 1450 ºC.

The low kinetics for solid solution formation in this ceramic material is responsible for its low sinterability.

Table 1 lists the relative density values obtained for several experimental conditions used in this work.

Table 1: Values of relative density for SDC1 specimens sintered at several conditions.

Conditions	Relative density (%)
1300 ºC/0 h	90.06 ± 0.98
1300 ºC/0 h + 1050 ºC/5 h	92.16 ± 0.70
1300 ºC/0 h + 1200 ºC/5 h	92.29 ± 0.98
1300 ºC/0 h + 1250 ºC/5 h	92.86 ± 084
1300 ºC/0 + 1275 ºC/5 h	92.44 ± 1.26
1450 ºC/0 h	93 ± 0.98
1450 ºC/0 h + 1200 ºC/5 h	94.53 ± 1.36
1450 ºC/0 h + 1300 ºC/5 h	94.12 ± 0.80
1450 ºC/0 h + 1350 ºC/5 h	93.14 ± 1.12
1450 ºC/0 h + 1400 ºC/5 h	92.72 ± 0.84

Results in Table 1 shows that the relative density of SDC1 specimens does not change significantly with the dwell temperature. The maximum density is already attained during the first step of sintering. For lower peak temperatures the final density is always lower meaning that no (or negligible) additional densification occurs in the second step of sintering.

Fig. 3 shows X-ray diffraction patterns of SDC1 and SDC2 specimens sintered at several temperatures.
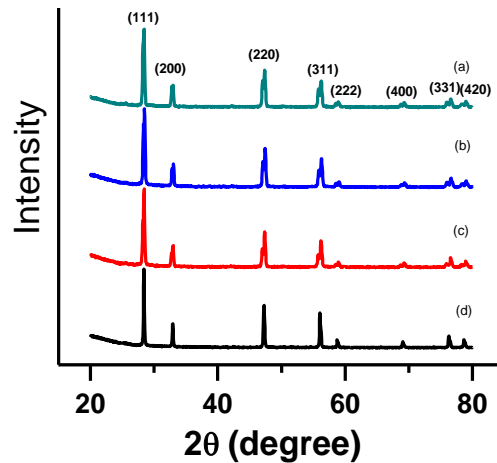
Fig. 3: X-ray diffraction of SDC1 and SDC2 sintered specimens.(a) SDC2-1500 °C /0 h, (b) SDC2-1450 °C /0 h + 1300 °C /5 h, (c) SDC2-1450 °C /0 h, (d) SDC1-1450 °C /0 h.

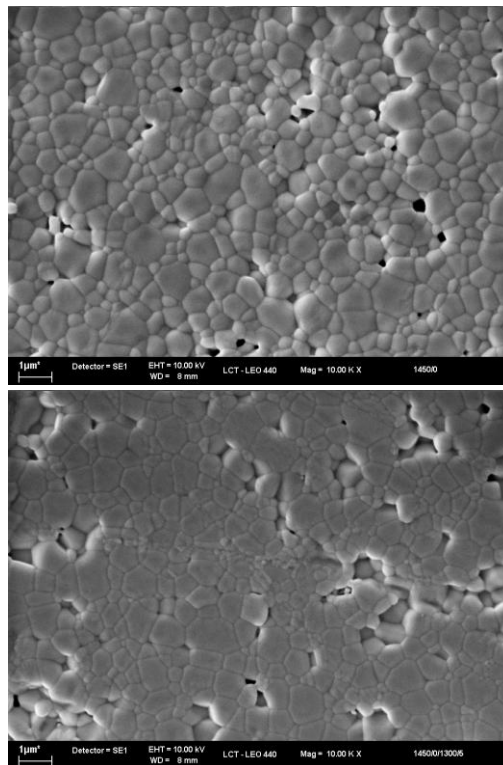All diffraction patterns are similar to that of cerium oxide (ICDD 34-394).

Fig. 4: SEM micrographs of sintered SDC1 specimens. Sintering conditions: 1450ºC/0 h (top), and 1450ºC/0 h + 1300ºC/5 h (bottom).

Small grains (< 1 μm) predominate in both SEM micrographs. The average grain size determined by the intercept method is 0.85 ± 0.02 μm (1450ºC/0 h) and 0.845 ± 0.012 μm (1450ºC/ 0h + 1300ºC/5 h). These results show that the second step of sintering does not contribute for densification neither for grain growth in samaria-doped ceria.

Fig. 5 shows Arrhenius plots of the grain (a) and grain boundary (b) conductivity.
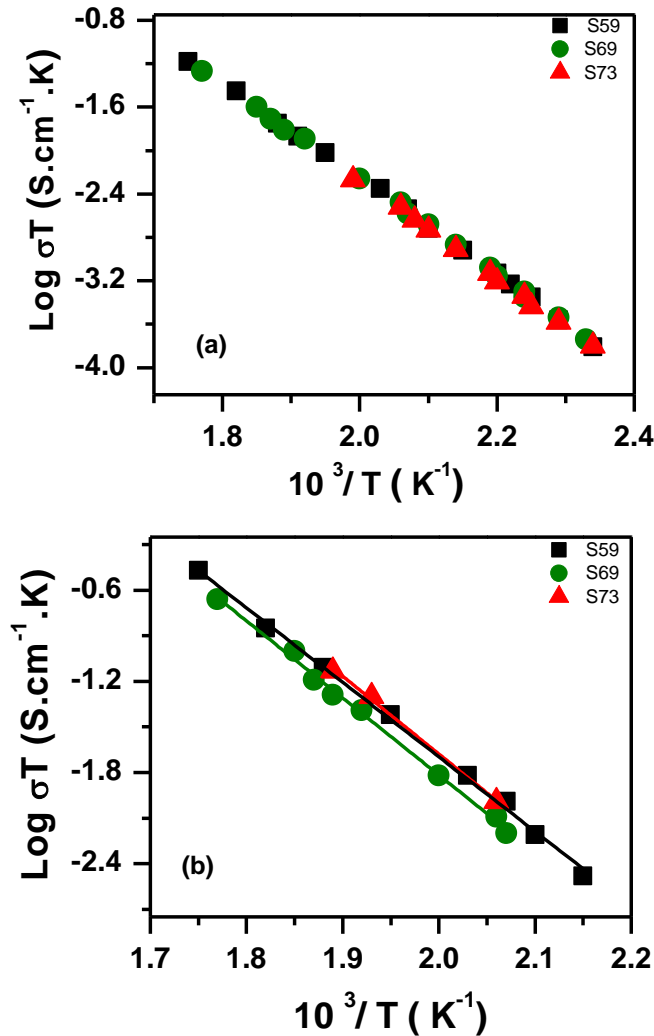
Fig. 5: Arrhenius plots of the grain (a) and grain boundary (b) conductivity of some SDC1 sintered specimens. S59 = 1450ºC/0 h + 1300ºC/5 h; S69 = 1300ºC/0 h + 1250ºC/5 h; S73 = 1450ºC/0 h.

The grain conductivity of sintered specimens does not depend on the sintering condition. The grain boundary conductivity depends on the grain size. The average grain size of specimen S69 (0.54 ± 0.01 μm) is considerably lower than that of other specimens (~ 0.85 μm). Then, decrease of the grain size results in increasing grain boundary area and in the blocking effect, thereby decreasing the grain boundary conductivity.

Conclusions

The density values obtained for specimens prepared with the commercial powder are always higher than those obtained for samples prepared by solid state reactions for the same sintering temperature. The electrical conductivity of grains does not change with the sintering profile. The grain boundary conductivity decreases with decreasing the sintering temperature due to the blocking effect of grain boundaries. The grain size is determined by the peak temperature. The two-step sintering process is not effective to reduce the sintering temperature of samaria-doped ceria.

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