Synthesis and Characterization of Gadolinia-Doped Ceria with Manganese Addition

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Abstract. Ceria-based materials have been extensively studied due to their wide range of technological application. In this work, nanostructured powders of 20 mol% gadolinia-doped ceria pure and containing 1 mol% manganese were synthesized by the cation complexation technique. Powder materials were calcined at 600ºC, uniaxially pressed and sintered in the 1200-1500ºC range for soaking times of 1, 2 and 4 h. X-ray diffraction patterns evidenced a single-phase fluorite-like structure in all studied specimens. The evolution of grain sizes was evaluated by scanning electron microscopy on polished and thermally etched surface of sintered pellets. The relative density decreases for soaking times above 1300ºC (with Mn) and 1400ºC (without Mn). The grain size increases with manganese addition. The role of the additive on the electrical conductivity of gadolinia-doped ceria was evaluated by impedance spectroscopy measurements.

Introduction

Cerium oxide (CeO_2) has been widely investigated over the last years because of its application in several technological areas. It has been used, for example, as component in three-way automotive catalysts and in other catalytic processes [1,2], as glass polishing material [3], gas sensor [4], UV absorbent [5], and as electrolyte and/or electrode components in electrochemical devices [6,7].

Cerium (IV) oxide has a cubic fluorite-type lattice (space group *Fm3m*) and exhibits relatively high hardness and reactivity [8]. Nominally pure ceria is an *n*-type semiconductor, although minor impurity contents are responsible for a low-conductivity extrinsic behavior. Additions of rare earth oxides to cerium oxide results in high ionic conductivity and the solid solutions may be used in solid oxide fuel cells.

In spite of its high reactivity, the densification of ceria and ceria-based materials is poor [9], and several approaches have been used to overcome this problem, such as the use of nanosized powders and the introduction of sintering aids. Among the transition metal cations, Co was shown to produce high densification at relatively low temperatures, whereas Mn was effective above 1050ºC [10] in gadolinia-doped ceria. The effect of Mn-addition on densification of cerium oxide has been studied [11-14], but some aspects are not well understood. Electrical conductivity measurements show that part of the Mn ions form solid solution with CeO_2, whereas diffuse reflectance infrared spectra (DRIFT) indicate that a fraction of the Mn cations remains segregated onto particles surface in chemically prepared powders [13]. The solubility limit of Mn in cerium oxide estimated by X-ray diffraction is between 5 and 10 mol%. The characteristic conductivity behavior depends on the Mn content being a single- or a dual-phase electronic conductor below and above the solubility limit, respectively [14].

In this work, the addition of 1 mol% Mn to 20 mol% gadolinia-doped ceria was investigated aiming an optimization of the synthesis process, in order to obtain better chemical homogeneity, good densification and microstructural homogeneity. The effect of manganese on the electrical conductivity of gadolinia-doped ceria was studied by impedance spectroscopy.

Experimental

Cerium nitrate hexahydrate, $Ce(NO_3)_3.6H_2O$, (99.9%, Strem Chemicals), gadolinium oxide, Gd_2O_3, (99.9%, Alfa Ventron) and manganese carbonate, $MnCO_3$ (99.9%, Alfa Aesar) were used as starting materials. The solid solution containing 20 mol% gadolinia and 1 mol% manganese (metal basis) was prepared by the cation complexation technique. For comparison purposes, the solid solution of 20 mol% gadolinia (GDC) containing ceria without manganese was prepared by the same technique. A full description of this method of synthesis and parameters used in the synthesis may be found in previous works [15,16]. In a typical experiment a citric acid ($C_2H_6O_2$, 99.5%, Synth) solution was added to the metal solution and the resulting mixed clear solution was heated up to a mild temperature of 80ºC. Continuous stirring of the precursor solution resulted in a sponge-like resin.

The temperature of the resin was obtained from thermogravimetric analysis (Netzsch, STA409). The solid solution was pressed into pellets by uniaxial and isostatic pressing. sintering was carried out at 1200, 1300, 1400 and 1500ºC for 1 h.

The sintered density was determined by the water immersion method. Phase characterization was accomplished by X-ray diffraction (D8 Advance, Bruker-AXS) using a Ni filtered Cu K_α radiation in the 20-80º 2θ range. Morphology of samples was observed by scanning electron microscopy (SEM, Philips, XL 30) using secondary electrons. The average grain size of sintered pellets was estimated by the intercept method [17]. 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 show thermogravimetric and thermodiferential curves for the resin containing 1 mol% Mn- and 20 mol% gadolinia-doped ceria.

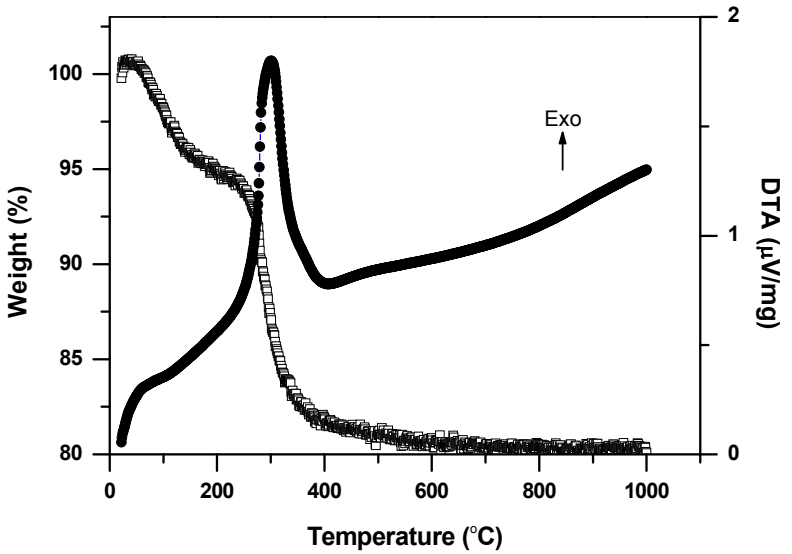


Fig. 1: Thermogravimetric and thermodiferential curves of the resin containing 1 mol% Mn- and 20 mol% Gd-doped ceria.

Two-stages of weight loss are clearly seen. The first one (70-180ºC) amounts ~ 5% and is related to water loss from the hygroscopic resin. The second step extends from ~ 250 to 390ºC resulting in about 13% of weight loss. This last stage of weight loss is due to the thermal decomposition of the organic material and results in an exothermic event. The residual organic material is burned out in the 400-600ºC range. Then, the temperature for calcination

of the resin was chosen as 600ºC. Total amount of weight loss was ~ 19%. Similar results were obtained for the resin without manganese.

Calcination at 600ºC for 1 h resulted in white nanopowders. Fig. 2 shows the X-ray diffraction pattern of the calcined material.

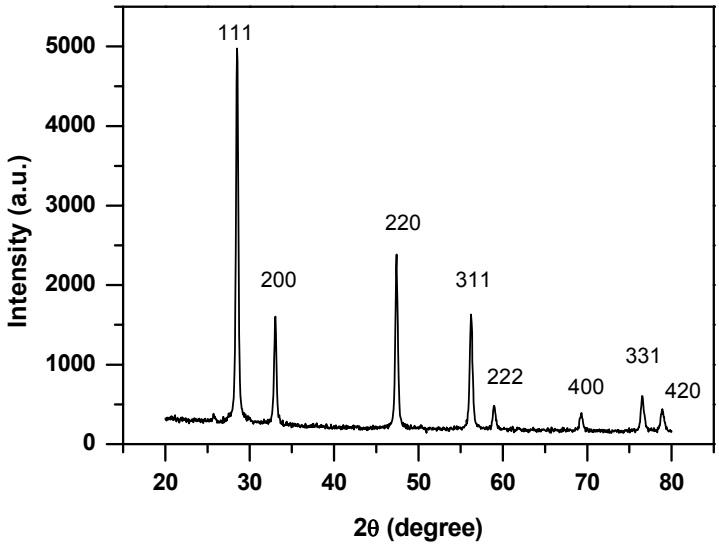


Fig. 2: X-ray diffraction pattern of 1 mol% Mn- 20 mol% Gd-doped ceria nanopowder.

The X-ray diffraction pattern is similar to that of CeO_2 and was indexed according to JCPDF 34-394 file. No evidence of isolated Mn or other compounds was detected. This result shows that a single fluorite-like phase material can be obtained at a mild temperature using this method of synthesis.

Table 1 list values of apparent density determined by the immersion method for specimens sintered at 1200ºC for different soaking times.

Table 1: Values of apparent density (in $g.cm^{-3}$) for specimens with and without Mn sintered at 1200ºC for several soaking times.

Specimen	1 h	2 h	4 h
GDC	6.7	7.2	7.3
GDC+1 mol% Mn	6.1	6.5	6.2

The sintered density increases with soaking time for GDC and Mn-containing GDC specimens. High values of density with short soaking times at 1200ºC were obtained for GDC specimen. This result shows that the method of synthesis favored the densification, probably because the calcined nanopowder obtained in this case has a narrow distribution of particle sizes [16].

Table 2 list values of apparent density obtained for specimens sintered at different dwell temperatures and soaking time of 4 h.

Table 2: Values of apparent density (in $g.cm^{-3}$) for specimens with and without Mn sintered at several dwell temperatures and 1 h of soaking time.

Specimen	1200ºC	1300ºC	1400ºC	1500ºC
GDC	6.7	7.2	7.3	6.8
GDC+1 mol% Mn	6.1	7,1	6.6	5.1

The sintered density of GDC increases for dwell temperatures up to 1400ºC and then decreases. For Mn-containing GDC the density increases up to 1300ºC and beyond that temperature decreases drastically.

Fig. 3 shows SEM micrographs of specimens sintered at 1300ºC for 4 h.

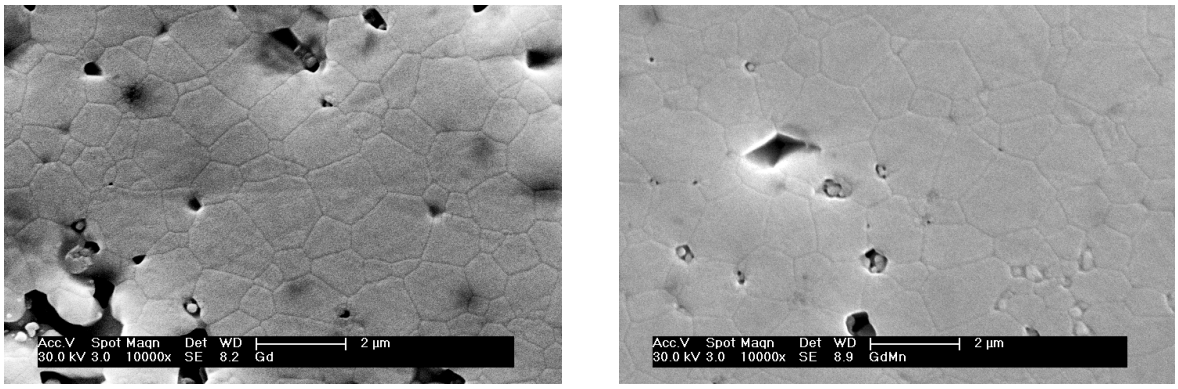
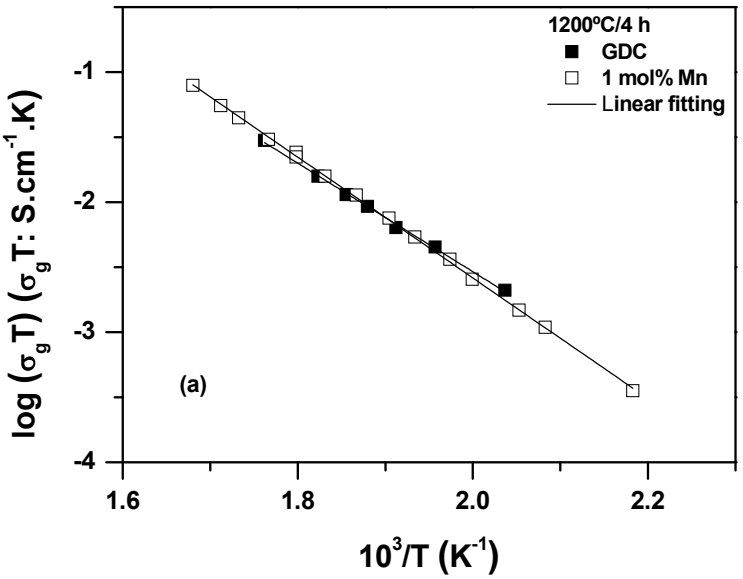


Fig. 3: SEM micrographs of specimens GDC (left) and 1 mol% Mn-doped GDC (right) sintered at 1300ºC for 4 h.

The main microstructural features are polygonal grains and low porosity. Most of pores are seen at the grain boundaries and triple junctions. The mean grain size values determined by the intercept method are 0.79 (GDC) and 0.92 µm (1 mol% Mn-doped GDC). Increasing the dwell temperature to 1400ºC, the mean grain size reach 1.80 (GDC) and 2.48 µm (1 mol% Mn-doped GDC). These results show that manganese promotes grain growth even for small contents. At 1200ºC de mean grain size of both specimens is similar: (0.43 µm, GDC and 0.45 µm, 1 mol% Mn-doped GDC).

The electrical conductivity of the prepared specimens was determined by impedance spectroscopy measurements. Fig. 4 shows, as an example, the grain conductivity, σ_g, of sintered specimens.



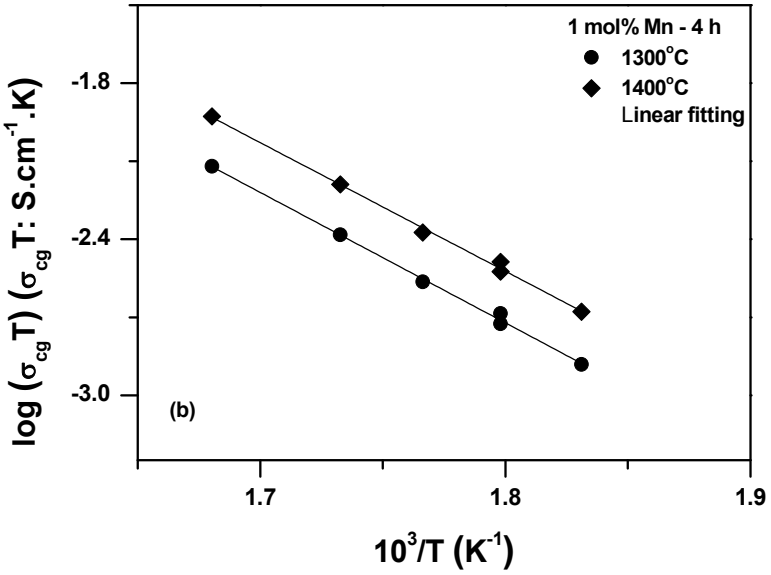


Fig. 4: Arrhenius plots of the (a) grain conductivity of specimens sintered at 1200ºC/4 h and (b) grain boundary conductivity of specimens sintered at several dwell temperatures.

The grain conductivity of specimens sintered at 1200ºC/ 4 h (a) is essentially unchanged with addition of manganese. This result evidences that 1 mol% manganese addition to gadolinia-doped ceria does not influence significantly the grain contribution of the total electrical conductivity. The same holds for other dwell temperatures and times. The grain boundary conductivity, however, is greatly enhanced with Mn addition. For pure gadolinia-doped ceria, this component of the total electrical conductivity could not be analyzed in details because of the huge grain boundary resistivity. This effect is assumed to the produced by the use of low purity starting materials. The grain boundary conductivity of some sintered specimens containing manganese (b) increases with increasing the dwell temperature. These results evidences that Mn added to gadolinia-doped ceria segregates at the grain boundaries, at least partially, and enhances the grain boundary conductivity either by creation of additional oxygen vacancies at the boundaries or by minimizing the deleterious effect of silicon at the interfaces. The exact mechanism of manganese on the grain boundaries of gadolinia-doped ceria is presently unknown and further studies are necessary.

Conclusions

The density values obtained for pure GDC specimens are always higher than those obtained for samples containing manganese for the same sintering temperature. Manganese addition to gadolinia-doped ceria promoted the grain growth of sintered samples. The electrical conductivity of grains does not change with the additive. The grain boundary conductivity is enhanced for Mn-containing GDC evidencing the segregation of the additive at the interfaces.

Acknowledgements

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