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Electrolyte materials for solid oxide fuel cells derived from metal complexes: Gadolinia-doped ceria

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Abstract

Gadolinia doped ceria (GDC) powders with different gadolinium contents were successfully prepared by the thermal decomposition of ceria complexes. All the calcined powder samples were found to be ceria-based solid-solutions having a fluorite-type structure. The powders were cold-isostatically pressed and sintered in air at 1500 °C for 5 h to attain a sintered density of about 90% of its theoretical value. The electrical conductivity of the GDC pellets in air was studied as a function of temperature in the 225–700 °C range, by using two-probe electrochemical impedance spectroscopy measurements. The highest total conductivity ($\sigma_{600\,^{\circ}\mathrm{C}} = 0.025$ S/cm) was found for the $Ce_{0.85}Gd_{0.15}O_{1.925}$ composition.

Keywords: A. Powders: chemical preparation; C. Ionic conductivity; D. CeO_2; E. Fuel cells

1. Introduction

Solid oxide fuel cells (SOFCs) using oxygen-ion conducting electrolytes offer a low-pollution technology to directly convert chemical energy into electricity with high efficiency [1]. The advantages of SOFCs over other conventional energy conversion systems include high efficiency, modularity, fuel adaptability, and very low levels of emissions depending on the fuel used [2]. However, SOFC operation needs elevated temperatures, above 900 °C, due to the use of yttria-stabilized zirconia (YSZ) as the electrolyte material, which results in high costs and in decreasing the durability, due to electrode sintering and interfacial reactions. Improved durability, a wider choice for interconnecting material selection, and lower costs can be achieved by reducing the operating temperature below 700 °C [3].

For this purpose, electrolytes with high oxygen-ion conductivity at low temperatures are under investigation. Moreover, reducing the electrolyte thickness decreases the electrolyte ohmic resistance. Gadolinia-doped ceria (GDC) is an attractive electrolyte alternative to YSZ, owing to its superior oxygen ion conductivity at low temperatures [4,5]. Ceria doping is needed to increase the oxygen vacancy concentration and to reduce the intrinsic electronic conductivity. Among the various doping elements investigated, Gd^{3+} and Sm^{3+} doped ceria (GDC and SDC) were reported to have the largest conductivity [6]. Moreover, studies have been carried out on co-doped ceria [7–10].

Currently, the common synthesis routes to prepare doped ceria powders include solid-state reaction [11,12], co-precipitation reaction [12–15], hydrothermal synthesis [16] and sol–gel routes [17]. However, these synthesis routes have some

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disadvantages, such as the cost of the starting materials, complexity, slowness, lack of homogeneity and purity, and high processing temperature. SOFC electrolyte materials usually possess complex compositions with several metallic elements, and therefore selecting a simple and low-cost method to effectively prepare doped ceria powders has distinct advantages for SOFC research.

In a previous work, Laobuthee et al. used a simple and straightforward method to directly prepare Mg–Al–TEA complex from $Al(OH)_3$, MgO and triethanolamine (TEA), as a precursor for magnesium aluminate spinel ($MgAl_2O_4$) via the oxide one pot synthesis (OOPS) process [18]. The obtained $MgAl_2O_4$, exhibiting high purity and homogeneity, was tested as a humidity sensor material [18]. However, this method showed some disadvantages, such as the limited solubility of the starting materials, the high boiling point of the ethylene glycol solvent, and the required reaction temperature at 200 °C. To address these limitations, based on the OOPS process, the nitrate salts were alternatively used as starting materials. Lower boiling point solvents, such as propan-1-ol and butan-1-ol, were also used to replace ethylene glycol. The complexes prepared by modified method were used as precursors for the production of high quality GDC powders, which were sintered into pellets and then characterized their electrochemical properties.

2. Experimental

The starting materials were cerium(III) nitrate hexahydrate [$Ce(NO_3)_3 \cdot 6H_2O$, 99.5% purity] and gadolinium(III) nitrate pentahydrate [$Gd(NO_3)_3 \cdot 5H_2O$, 99.9% purity], purchased from Acros Organics. Triethanolamine [TEA, $N(CH_2CH_2OH)_3$, 98% purity] and propan-1-ol [$CH_3CH_2CH_2OH$, 99.5% purity] were obtained from Carlo Erba (Barcelona). All chemicals were used as provided.

The complexes were prepared by mixing in 80 mL propan-1-ol, $Ce(NO_3)_3 \cdot 6H_2O$ and $Gd(NO_3)_3 \cdot 5H_2O$, with the molar ratios of Ce:Gd = 0.9:0.1, 0.85:0.15, and 0.8:0.2, denoted $Ce_{0.9}Gd_{0.1}O_{1.95}$, $Ce_{0.85}Gd_{0.15}O_{1.925}$, and $Ce_{0.8}Gd_{0.2}O_{1.9}$, respectively. TEA was added in the 1:1 molar ratio of metal ions to TEA. After amalgamation, the as-prepared transparent solutions were distilled for 3 h in order to obtain the complex precipitates. The precipitates were collected by filtration and then washed with propan-1-ol. Simultaneous thermogravimetric and differential thermal analysis (TG/DTA) of the complexes was performed using a TGA/SDTA analyzer (Model TGA/SDTA 851e, Mettler Toledo), in flowing air with a heating rate of 5 °C/min, in the 50–1000 °C temperature range.

The complexes were calcined in an alumina crucible at various temperatures: 400, 600, 800, 1000, and 1200 °C for 2 h. Phase identification was performed using X-ray diffraction analysis (XRD; Philips X-Pert-MPD X-ray diffractometer) operating at 40 kV/30 mA, with monochromated Cu Kα radiation. Diffraction patterns were recorded in the range of $2\theta = 20–90^\circ$ by step-scanning, with a step interval of 0.02° and a scanning time of 2 s for each step.

The specific surface area of the powders, S_{BET}, was measured using the Brunauer–Emmett–Teller (BET) nitrogen-gas absorption method. The values were calculated from the nitrogen absorption isotherms at 77 K, using a Micromeritics ASAP 2020 surface analyzer at a value of 0.162 nm^2 for the cross-section of the nitrogen molecule. Samples were degassed at 350 °C under high vacuum conditions for 20 h before measurements. The specific surface area was converted to particle size (D_{BET}) according to Eq. (1), under the approximation that the particles were closed spheres with a smooth surface and of uniform size.

$$D_{BET} = \frac{6 \times 10^3}{d_{th} S_{BET}} \quad (1)$$

Here, d_{th} was the theoretical density of the material (g/cm^3) and D_{BET} was the average particle size (nm). The specific surface area, S_{BET}, was expressed in m^2/g.

Scanning electron micrographs were obtained using a JEOL JSM-6301F scanning electron microscope (SEM) operating at an acceleration voltage of 12 kV, to identify the powder microstructure. Samples were mounted on aluminum stubs using carbon tape and then sputter coated with Au to avoid particle charging.

The obtained powders were uniaxially pressed into green pellets (~30 MPa) in a stainless steel die of 10 mm in diameter, and then isostatically pressed at ~200 MPa. When not specified, the powders used were those calcined at 600 °C. Dense pellets were prepared by sintering the green pellets at 1500 °C for 5 h with a ramp rate of 3 °C/min and naturally cooled in the furnace. The relative density of the sintered pellets was determined using the Archimedes' principle. Powder XRD analysis was performed on polished samples.

Electrodes were painted using a gold paste onto both sides of the pellets, and fired at 800 °C for 2 h. The pellets were placed in an alumina holder using a spring-clip arrangement between Pt current collectors. The electrochemical impedance spectroscopy (EIS) measurements were performed from 0.1 Hz to 10 MHz, using a Solartron 1260 impedance/gain phase analyzer, interfaced to a personal computer, and run through ZPlot® and Zview software (Scribner Associates, Incorporated); 10 points were taken per decade of frequency. The amplitude of the AC signal imposed on the samples was 10 mV. The EIS measurements were performed at controlled temperatures in the 225–700 °C range.

3. Results and discussion

The various complexes between $Ce(NO_3)_3$, $Gd(NO_3)_3$, and TEA were prepared in propan-1-ol. Yellowish powders were obtained, although the contents of Ce^{3+} and Gd^{3+} varied. The yellowish powders were precipitated when the complexes completely reacted in propan-1-ol for 3 h.

To obtain the ceramic powders, the complexes were calcined to remove the organic contents. The appropriate temperature for calcination was studied using TG/DTA measurements. Fig. 1, as an example, shows the TG/DTA curves of the complex for 10 mol% GDC. The broad endothermic peak, centered at ~100 °C on the DTA curve, was mainly caused by the loss of

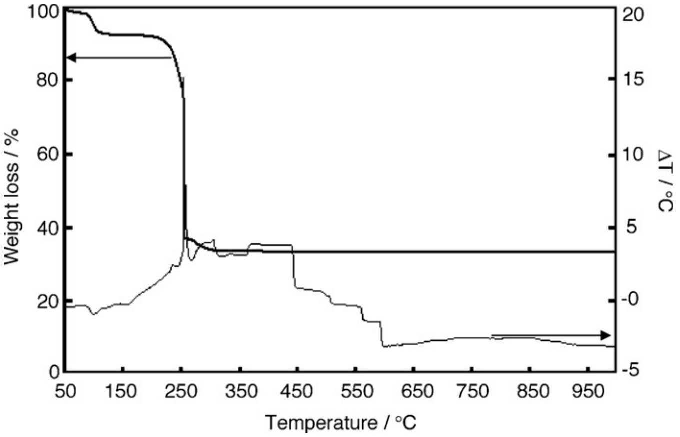

Fig. 1. TG and DTA curves of a 10 mol% doped gadolinium CeO_2 complex.

Table 1
Specific surface area (S_{BET}) and average particle size (D_{BET}) of $Ce_{0.9}Gd_{0.1}O_{1.95}$, $Ce_{0.85}Gd_{0.15}O_{1.925}$, and $Ce_{0.8}Gd_{0.2}O_{1.9}$ powders calcined at various temperatures.

Sample	T (°C)	Specific surface area, S_{BET} (m^2/g)	D_{BET} (nm)
$Ce_{0.9}Gd_{0.1}O_{1.95}$	600	23.6	35
	800	19.2	43
	1000	7.5	111
$Ce_{0.85}Gd_{0.15}O_{1.925}$	600	28.6	29
	800	15.0	55
	1000	7.8	106
$Ce_{0.8}Gd_{0.2}O_{1.9}$	600	22.1	38
	800	12.9	65
	1000	8.6	97

physisorbed water and propan-1-ol. The sharp exothermic peak with its maximum at 250 °C, accompanied by an abrupt weight loss in the TG curve, was caused by the decomposition of the organic ligand and generated char as a by-product. A slight weight loss together with broad exothermic effects was observed in the 300–600 °C temperature range, which was ascribed to the burning of the residual organic components. Above 600 °C, no weight loss was observed, showing that the appropriate calcination temperature for the preparation of the ceramic powders is likely to be 600 °C.

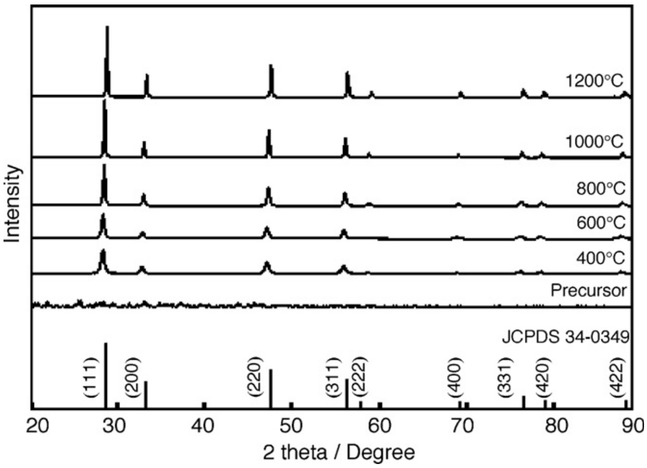

Fig. 2. XRD patterns of the 20 mol% doped gadolinium CeO_2 complex and $Ce_{0.8}Gd_{0.2}O_{1.9}$ powders calcined between 400 and 1200 °C.

Based on the TG/DTA analysis, the complexes were calcined at 400, 600, 800, 1000 and 1200 °C for 2 h in air. The obtained products were light-yellowish colored powders. XRD was used to characterize the powders. Fig. 2 shows the XRD patterns of the $Ce_{0.8}Gd_{0.2}O_{1.9}$ powders at various heating temperatures. Before calcination, all the complexes exhibited low crystallinity. In agreement with the results of TG/DTA analysis, the powders of each complex calcined at 600 °C for

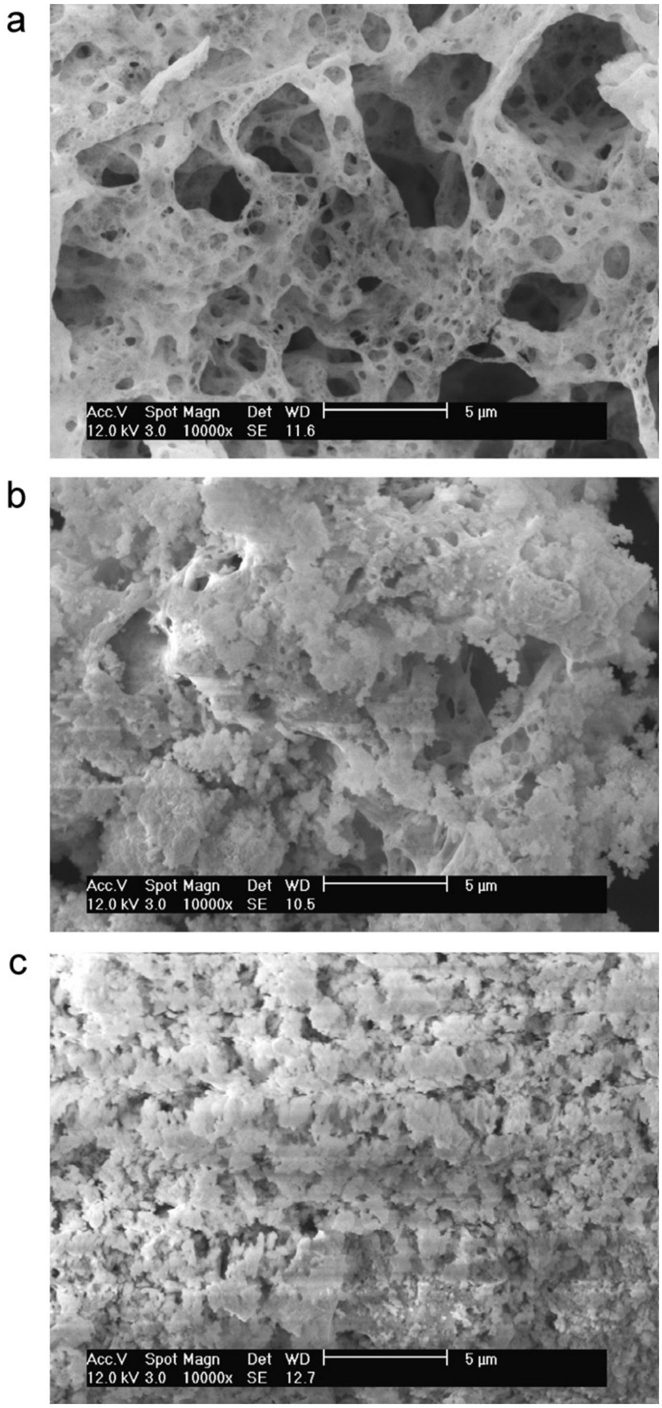

Fig. 3. SEM micrographs of the $Ce_{0.8}Gd_{0.2}O_{1.9}$ powder calcined at (a) 600 °C, (b) 800 °C and (c) 1000 °C.

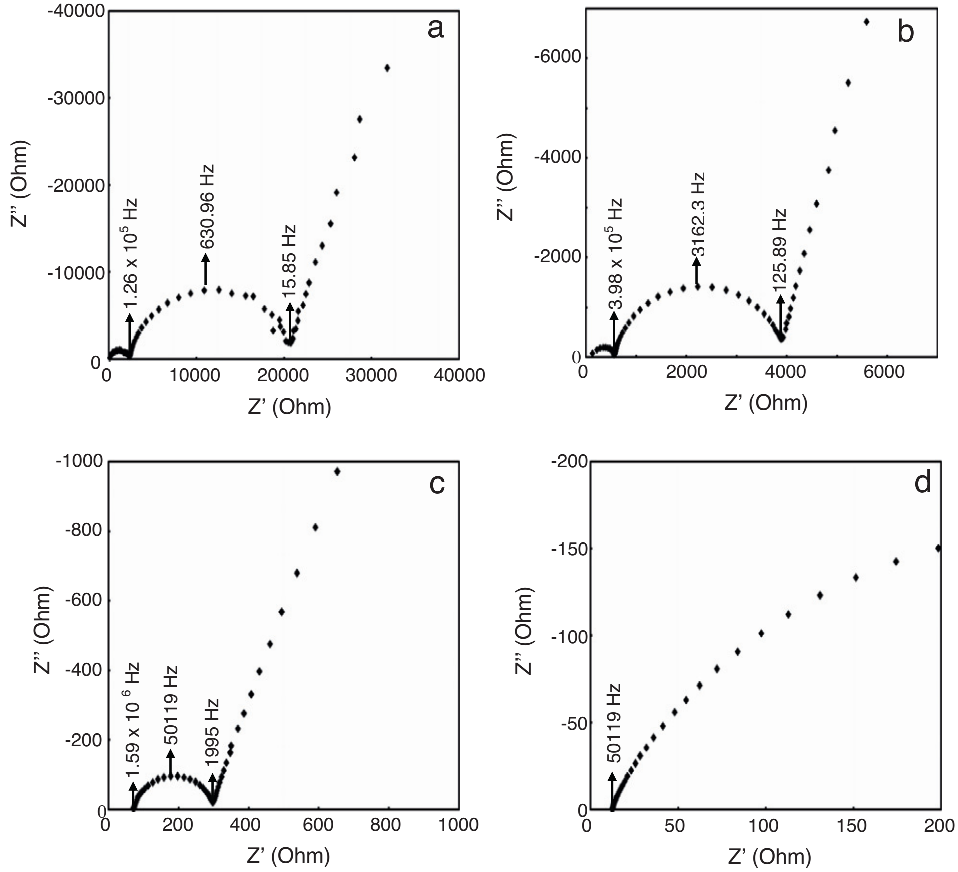

Fig. 4. Complex impedance plane plots of $Ce_{0.85}Gd_{0.15}O_{1.925}$ pellet sintered at 1500 °C, measured at (a) 250 °C, (b) 300 °C, (c) 400 °C and (d) 600 °C in air.

2 h displayed only reflections corresponding to the fluorite structure of CeO_2 (JCPDS Powder Diffraction File No. 34-0394). The diffraction peaks of each powder sample were sharper and narrower with increasing the heating temperature, indicating an increase in the crystallite size. The same trend was also observed for the $Ce_{0.9}Gd_{0.1}O_{1.95}$ and $Ce_{0.85}Gd_{0.15}O_{1.925}$ samples. No crystalline phases corresponding to Gd_2O_3 could be found at any calcination temperatures for the Gd-doped complexes, showing the direct formation of solid solutions.

Table 1 summarizes the specific surface area values obtained for the calcined powders. Table 1 also reports the average particle size (D_{BET}) of the powders calcined at 600, 800, and 1000 °C, which were calculated to be in the nanometer scale. As expected, the surface area decreased and the particle size increased with raising the calcination temperature.

Fig. 3 shows the typical SEM micrographs of the $Ce_{0.8}Gd_{0.2}O_{1.9}$ powders at selected heating temperatures. The powders showed a foam-like morphology at 600 °C. This is probably due to the fact that the decomposition products of the organic residues in the complexes, such as CO, CO_2, H_2O and volatile hydrocarbon, did not escape easily from the resulting powders. By increasing the calcination temperature up to 1000 °C, the powders were made of blocky particles with an irregular shape, due to agglomeration and sintering taking place during the thermal treatment. The particle size ranged from submicron to larger than 1 μm. Fine powders with low agglomeration were obtained heating the complexes at 600 °C.

The pellet samples, prepared using the powders calcined at 600 °C, were sintered at 1500 °C for 5 h to ensure a high

Table 2
Density (% of the theoretical density) and activation energy of bulk, grain boundary, and total conductivities for $Ce_{0.9}Gd_{0.1}O_{1.95}$, $Ce_{0.85}Gd_{0.15}O_{1.925}$, and $Ce_{0.8}Gd_{0.2}O_{1.9}$ pellets sintered at 1500 °C.

Sample	Density (% theoretical)	Activation energy (eV)		
		Bulk	Grain boundary	Total conductivity
$Ce_{0.9}Gd_{0.1}O_{1.95}$	93	0.92	0.97	0.91
$Ce_{0.85}Gd_{0.15}O_{1.925}$	94	0.82	0.96	0.78
$Ce_{0.8}Gd_{0.2}O_{1.9}$	94	1.02	1.08	0.94

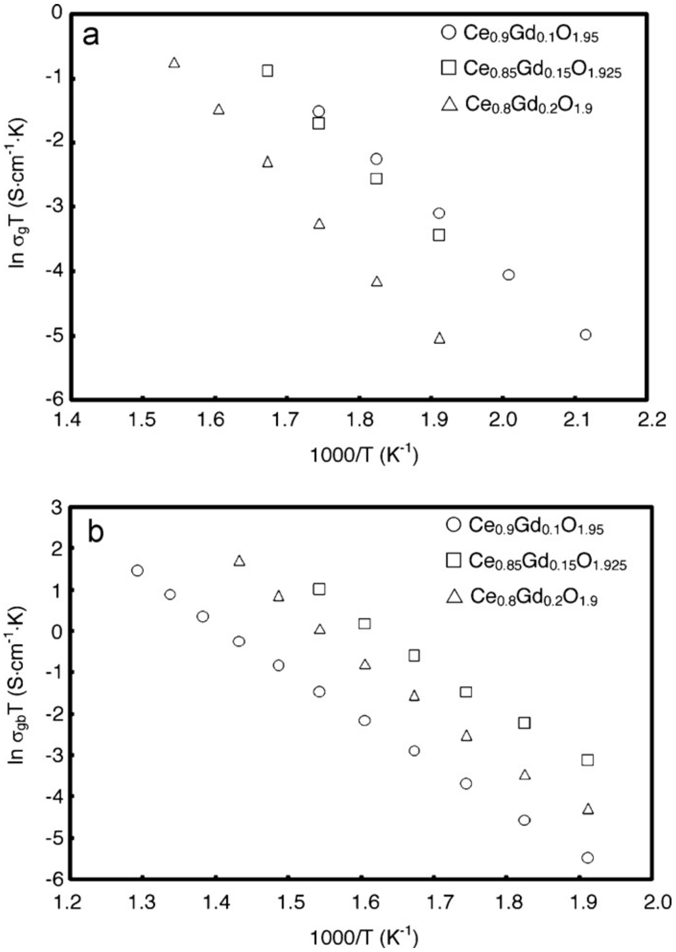

Fig. 5. Arrhenius plots of the (a) bulk and (b) grain boundary conductivity as a function of temperature for the $Ce_{0.9}Gd_{0.1}O_{1.95}$, $Ce_{0.85}Gd_{0.15}O_{1.925}$, and $Ce_{0.8}Gd_{0.2}O_{1.9}$ pellets.

density for electrical measurement. Phase identification was confirmed by XRD. The density of the pellets was more than 90% of the theoretical density before measurement, as shown in Table 2.

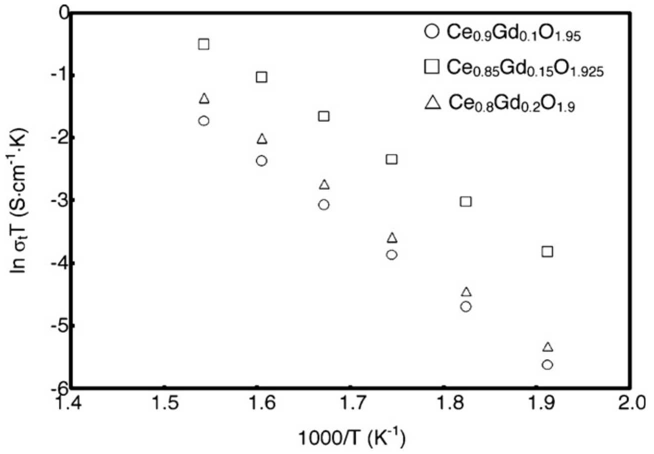

Fig. 6. Arrhenius plots of the total conductivity of the $Ce_{0.9}Gd_{0.1}O_{1.95}$, $Ce_{0.85}Gd_{0.15}O_{1.925}$ and $Ce_{0.8}Gd_{0.2}O_{1.9}$ pellets.

Fig. 4 shows the typical complex impedance plane plots of the $Ce_{0.85}Gd_{0.15}O_{1.925}$ pellet measured at (a) 250 °C, (b) 300 °C, (c) 400 °C, and (d) 600 °C. Two well-defined semicircular arcs were observed below 300 °C, which became one semiarc below 400 °C, accompanied by a spike at low frequencies. At higher temperatures, a single spike was observed. The same trend was observed for all the samples examined. The features in the impedance plots can be attributed to the contribution of the bulk (B) at high frequencies, the grain boundary (GB) at intermediate frequencies, and electrode

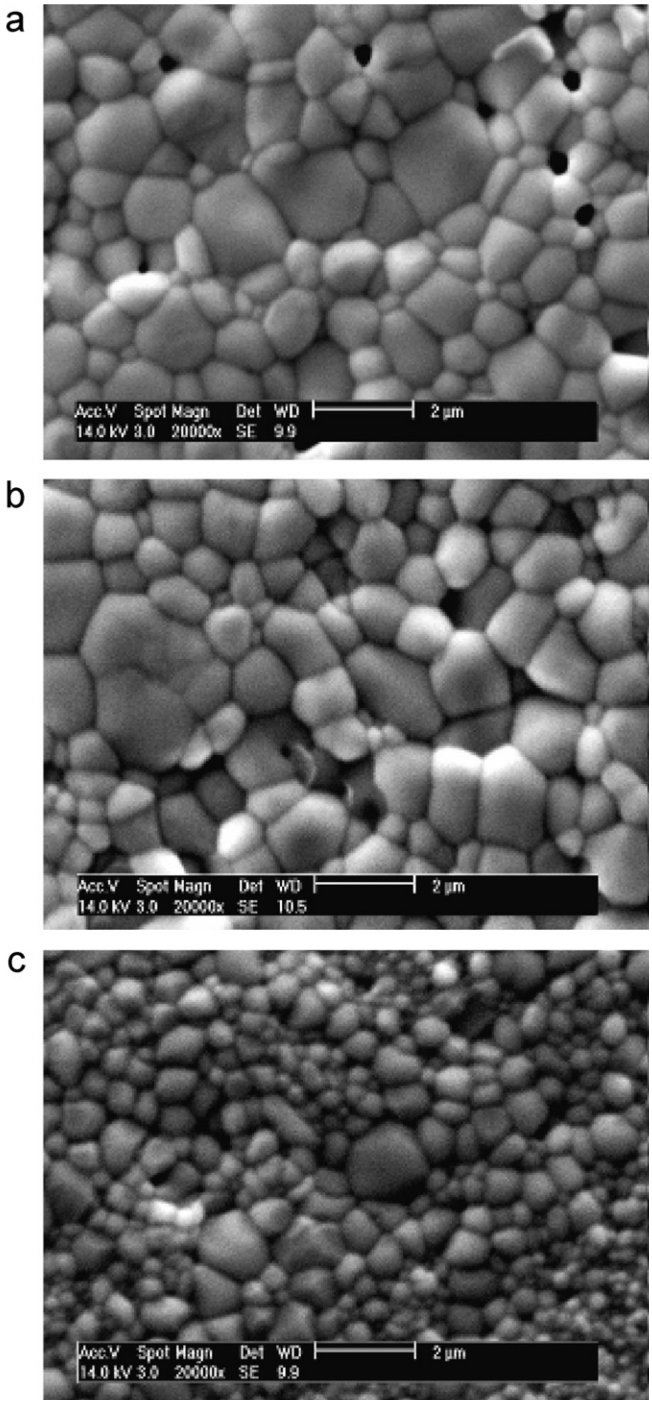

Fig. 7. SEM micrographs of (a) $Ce_{0.9}Gd_{0.1}O_{1.95}$, (b) $Ce_{0.85}Gd_{0.15}O_{1.925}$, and (c) $Ce_{0.8}Gd_{0.2}O_{1.9}$ pellets sintered at 1500 °C for 5 h.

polarization (E) at low frequencies, based on different relaxation frequency and capacitance values. The impedance behavior of $Ce_{1-x}Gd_xO_{2-(x/2)}$ ceramic pellets was similar to the trend usually observed for polycrystalline ceramic materials, as frequently documented in the literature [12].

Fig. 5(a) and (b) shows the Arrhenius plots of the apparent grain conductivity, σ_g, and the grain boundary conductivity, σ_{gb}, respectively, for $Ce_{0.9}Gd_{0.1}O_{1.95}$, $Ce_{0.85}Gd_{0.15}O_{1.925}$, and $Ce_{0.8}Gd_{0.2}O_{1.9}$ samples. The values were obtained from the EIS measurements.

It has been shown that oxygen-ion conductivity in rare earth (Re^{3+}) doped ceria can be represented by the following equation (2):

$$\sigma = \left(\frac{A}{T}\right)\exp\left(\frac{-E_a}{k_B T}\right) \tag{2}$$

One can observe that the bulk conductivity (σ_b) of the $Ce_{1-x}Gd_xO_{2-(x/2)}$ samples followed the order: $x = 0.1 > 0.15 > 0.2$, which is in agreement with the results documented in the relevant literature [6]. This is in line with expectations, because the increase in dopant concentration beyond $x = 0.1$ results in defect association, which in turn decreases the ionic conductivity. However, the grain boundary conductivity (σ_{gb}) of the $Ce_{1-x}Gd_xO_{2-(x/2)}$ samples followed the order: $x = 0.15 > 0.2 > 0.1$, which shows that the grain boundary conduction can be improved by an increase in dopant concentration above 10 mol%.

Fig. 6 shows the temperature dependence of the total conductivity, σ_t, for $Ce_{1-x}Gd_xO_{2-(x/2)}$ solid solutions. The total conductivity of the $Ce_{1-x}Gd_xO_{2-(x/2)}$ samples reached a maximum at $x = 0.15$. Usually, the maximum conductivity is believed to result from two divergent effects: (i) gadolinium substitution, which causes a significant increase in oxygen vacancy concentration and thus a rise in the ionic conductivity; (ii) the interaction between oxygen vacancies, which leads to a decrease in the mobility of vacancies and a subsequent decrease in the ionic conductivity. However, according to our study, it appears that the grain boundary conductivity determines the maximum in the total conductivity at $x = 0.15$. Moreover, Table 2 gives the activation energy values for all the samples, and $Ce_{0.85}Gd_{0.15}O_{1.925}$ showed the smallest activation energy values.

Fig. 7 shows the SEM micrographs of (a) $Ce_{0.9}Gd_{0.1}O_{1.95}$, (b) $Ce_{0.85}Gd_{0.15}O_{1.925}$, and (c) $Ce_{0.8}Gd_{0.2}O_{1.9}$ pellets sintered at 1500 °C. For $Ce_{0.85}Gd_{0.15}O_{1.925}$ and $Ce_{0.8}Gd_{0.2}O_{1.9}$, dense pellets were obtained, but the $Ce_{0.85}Gd_{0.15}O_{1.925}$ pellet showed larger grains corresponding to a smaller grain boundary volume, which might be the reason for the larger total conductivity observed for 15 mol% Gd doped ceria.

4. Conclusions

$Ce_{1-x}Gd_xO_{2-(x/2)}$ ($0.1 \le x \le 0.2$) solid solutions having a fluorite structure were prepared by the metal organic complex method. Ultrafine particles were formed. The small particle size of the doped ceria powders allowed the sintering of dense ceramic pellets at 1500 °C, which was smaller than 1600 °C, the temperature required to sinter the corresponding materials prepared by the conventional solid state method. The largest conductivity was found for the $x = 0.15$ Gd substituted ceria ($\sigma_{600\,°C} = 0.025$ S/cm).

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