Optical and electrical characterization of samaria-doped ceria

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1. Introduction

Samaria-doped ceria (SDC) has received much attention over the last two decades due to its high ionic conductivity compared to the traditional yttria-stabilized zirconia solid electrolyte [1,2]. Hence, the last two decades due to its high ionic conductivity compared to the traditional yttria-stabilized zirconia solid electrolyte [1,2]. Hence, the use of SDC as electrolyte has been one of the main research goals.

Many efforts have been devoted to the synthesis of reactive and sinterable samaria-doped ceria powders using a number of solution techniques, and the characterization of the prepared nanomaterials has been focused on the electrical properties.

The preparation of doped-ceria powders may be carried out by means of inorganic methods such as precipitation and hydrothermal, as well as organic methods like the polymerized complex and the metallocorganic sol–gel. In every case, a thorough characterization of the produced material is recommended, because these methods give rise to different powder characteristics. Recently, for example, the particle size and the specific surface area of cerium oxide have been shown to vary considerably according to the preparation methods [3).

Precipitation or coprecipitation methods from salt solutions are by far the most employed, due to their high benefit to cost ratio [4]. The use of homogeneous precipitation for the synthesis of ceria-based powders has already been reported [5–8]. The main advantages attributed to this variant method include the control of particle size and shape, relatively high reactivity and sharp distribution of particle sizes [9].

Relatively few studies may be found on photoluminescence of samaria-doped ceria [10,11]. The great interest in research on rare earth-based luminescent materials is mainly owing to their potential technological applications [12] such as medical diagnostics, electroluminescence, optical markers and even laser materials, phosphors, fluorescent tubes, etc.

In a previous publication some physical characteristics of Ce1−xSmxO2−δ with 0 ≤ x ≤ 30 prepared by the homogeneous precipitation method using different solvents were reported [13]. It was shown that single-crystalline samaria-doped ceria nanoparticles of 5–8 nm in size can be directly obtained without the thermal decomposition step. Powder pellets attained high densification at relatively lower sintering temperatures, and the electrical conductivity was improved when compared to that of pellets prepared by the conventional solid state method.

In this work, characterization of Ce0.8Sm0.2O1.9 solid solution prepared by this modified homogeneous precipitation method will be focused. Special attention is given to chemical and structural properties of nanoparticles along with the electrical conductivity of sintered compacts. The photoluminescence properties of trivalent samarium ion introduced into the ceria matrix are also discussed in detail.
2. Experimental

2.1. Preparation method

Rare earth nitrates RE(NO$_3$)$_3$·6H$_2$O (99.99%, Aldrich, where RE$^{3+}$ = Ce$^{3+}$ and Sm$^{3+}$ ions) and hexamethylenetetramine (HMT (CH$_2$)$_6$N$_4$, 99%, Alfa Aesar) were used as starting materials without further purification. Stock solutions of RE$^{3+}$ nitrates (1.0 mol L$^{-1}$) were prepared by dissolving the starting materials in deionized water or in mixtures of water and alcohol (50%, v/v). The concentration of each stock solution was determined by complexometric titration using ethylenediaminetraacetic acid (EDTA) as complexant, buffer of acetic acid/sodium acetate to control the pH and xylenol as indicator. Three different alcohols were used: absolute ethanol (EtOH), iso-propanol (i-ProH) and tert-butanol (t-BuOH). Mixed cation solutions were prepared and the concentration was adjusted to 0.04 mol L$^{-1}$. Excess of HMT (0.5 mol L$^{-1}$) was added dropwise to the mixed rare earth nitrate solution, which was kept under vigorous stirring overnight at room temperature ($\sim$25 $^\circ$C). The colloidal dispersion was aged at 85 $^\circ$C for 1 h and cooled down to room temperature. Afterwards, the precipitate was washed with absolute ethanol and filtered through a 0.2 $\mu$m membrane. Further details of the experimental procedure were reported in Ref. [13]. The use of a mixture of alcohol and water as solvent promoted an increase in the filtration rate by a factor of 10 compared to that of powders prepared using only water as solvent. The precipitate was dried in an oven at 70 $^\circ$C for 24 h. For comparison purposes, nominally undoped CeO$_2$ sample was prepared by the same method. Afterwards, the precipitate was dried in an oven at 70 $^\circ$C for 24 h. The sintering of green compacts was carried out in air at several temperatures with holding time of 5 h.

2.2. Characterization techniques

The specific surface area (S) of calcined powders was determined by nitrogen adsorption (Micromeritics, ASAP2010) after degassing at 300 $^\circ$C using the BET model (Brunauer, Emmett and Teller). The apparent density of sintered pellets was determined by the water immersion method. Structural characterization was carried out by Raman spectroscopy (Renishaw Raman microscope system 3000) using the 632.8 nm exciting radiation of a 25 mW He–Ne laser (model 127, Spectra Physics). The actual Sm$^{3+}$ ion content was obtained from energy dispersive spectroscopy, EDS, analysis of sintered pellets. Microstructure observations were carried out by transmission electron microscopy, TEM (Philips, CM200). Excitation and emission photoluminescence (PL) spectra were recorded at room temperature, collected at an angle of 22.5$^\circ$ (front face) in a spectrofluorimeter (SPEX, Fluorolog 2) with double grating 0.22 mm monochromator (Spx 1680) and using a 450 W Xenon lamp as excitation source. The electrical conductivity was determined by impedance spectroscopy measurements using a low-frequency impedance analyzer (4192A Hewlett Packard) in the 5 Hz to 13 MHz frequency range. Silver paste was used as electrode material.

3. Results and discussion

It was shown earlier [13] that the powder materials prepared in EtOH/water solvent have high yield compared to other solvents. For a 50/50% (v/v) EtOH/water solvent the yield was about 50%, which may reach 80% for a 70/30% (v/v) mixture without changing the specific surface area or other properties of the nanoparticles. The following results were obtained for a 50/50% (v/v) alcohol/water solvent.

3.1. Chemical and structural characterization

Previous studies [1,14] on the composition-dependence of the electrical conductivity of samaria-doped ceria have shown that a maximum in the isothermal conductivity curve is obtained at 20 mol% SmO$_{1.5}$. In order to obtain that composition in the final material, powders containing different SmO$_{1.5}$ amounts were synthesized and used to obtain a calibration curve (Fig. 1) for determining the actual Sm$^{3+}$ content using energy dispersive spectroscopy analysis.

This result shows that the precipitation of Ce$^{3+}$ and Sm$^{3+}$ ions is not quantitative, as expected, due to the different rates of hydrolysis of both rare earth ions. This calibration curve (Fig. 1) was used to obtain the Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ Sample. Table 1 shows specific surface area values (S) determined from BET model for powder samples prepared in different alcoholic solvents and calcined at 450 $^\circ$C. The specific surface area varies with the type of solvent used for the synthesis. EtOH/water mixed solvent was found to give the highest S value, whereas t-BuOH/water resulted in the lowest S value. Assuming that the shape of the calcined particles may be approximated to spherical, an estimative of the particle size (d$_{BET}$) may be obtained using the equation: $S=6/d_{BET}^{2}\rho$, where $\rho$ is the crystallographic density. Table 1 shows that the particle sizes determined after calcination at 450 $^\circ$C are similar for powders synthesized using different solvents. Thus, in the absence of significant differences in the agglomeration degree, the densification of green compacts prepared with these powders might also be similar.

Fig. 2 shows a bright-field transmission electron microscopy micrograph (TEM) of Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ sample prepared in a mixed solvent.
solvent (EtOH/water) after calcination at 450 °C for 2 h. A crowded network of nanoparticles may be seen due to spontaneous agglomeration that occurs, owing to the small size of the particles. The estimated mean particle sizes after calcination at 450 and 700 °C are around 3 and 8 nm, respectively. The difference in the particle sizes in Table 1 and Fig. 2 reveals that each particle is composed by several primary particles.

Fig. 3 shows Raman spectra of CeO₂ and Ce₀.₈Sm₀.₂O₁.₉ nanoparticles prepared in a mixed solvent (i-PrOH/water) after calcination at 700 °C. The Raman spectrum of undoped cerium oxide (empty symbol) consists of a single active mode centered at 463 cm⁻¹ characteristic of this structure, which is attributed to a triple degenerate F₂g mode [15]. In samaria-doped ceria sample (full symbol) two additional low-intensity Raman bands were detected (≈510 and ≈630 cm⁻¹). These bands are usually assigned to the presence of extrinsic oxygen vacancies created as charge compensating defects during solid solution formation.

A linear relationship between the reciprocal of the particle size or the grain size in cerium oxide and the full width at half maximum (Γ) of the Raman band has been reported. Weber et al. [16] fitted their results to the equation \( Γ = 10 + 124.7/d \) (Å), where \( d \) is the particle size. Kosacki et al. [17] demonstrated a similar effect in CeO₂ thin films deposited over sapphire substrate. The fitting of their data resulted in the following equation: \( Γ = 5 + 518/d \) (Å), where \( d \) is the grain size. The determined values for the sample calcined at 700 °C using these equations resulted in particle sizes around 2 and 5 nm using the Weber and the Kosacki equations, respectively. These figures are far below the estimated size (∼8 nm) obtained by TEM, suggesting that variation in \( Γ \) should be interpreted as a parameter producing changes in the vibrational Raman mode, but not specifically the particle or the grain size. In effect, \( Γ \) is not but a coherence length [18] which may correspond to the grain size as well as to the size of cation domains in incommensurate phases, or to interspaces between defects or impurities or to a number of other parameters. The broadening of the Raman band with decreasing the calcination temperature corroborates previous results [17,18].

Fig. 4 shows the variation of \( Γ \) with the temperature of calcination and for non-calcined CeO₂. It can be seen that this parameter decreases linearly with increasing calcination temperature. Therefore, the variation of \( Γ \) in undoped cerium oxide polycrystalline samples follows the same trend as that in thin films, and is in some way related to the growth of the nanoparticles.

For Ce₀.₈Sm₀.₂O₁.₉ nanopowders calcined at several temperatures the \( Γ \) variation did not follow a linear relationship, in general agreement with Lin et al. [19] who studied the variation of the particle size with the temperature of thermal treatment by Raman spectroscopy and XRD, in sol–gel synthesized Ce₀.₈Nd₀.₂O₂₋₄. The reason for this is unclear and further experiments are necessary to clarify the role of the particle size in the variation of the full width at half maximum of the Raman band with the calcination temperature in doped ceria. It is also observed that the Raman peak position of Ce₀.₈Sm₀.₂O₁.₉ nanopowders around 447 cm⁻¹ shows a red-shift compared to CeO₂ sample (463 cm⁻¹), due to changes in the crystal environment by solid solution formation. Finally, \( Γ \) is larger for doped sample than for the undoped one, in agreement with results for single crystals of Gd³⁺-doped ceria [17].

3.2. Photoluminescence behavior

Luminescent materials containing rare earth ions based on the intraconfigurational 4f–4f transitions (forbidden by parity) have been extensively studied for exhibiting narrow emission bands [12,20]. Introduction of the trivalent cerium ion (Ce³⁺, 4f¹) into inorganic matrices, in contrast, gives rise to a broad and high intensity emission band in the blue-UV spectral range assigned to interconfigurational 5d → 4f transition allowed by the parity rule [21]. Moreover, the tetravalent cerium ion (Ce⁴⁺, 4f⁰) has an empty electronic configuration. The CeO₂ host exhibits a strong UV absorption arising from the ligand-to-metal charge-transfer states O → Ce⁴⁺ (LMCT) from O²⁻ ligand to Ce⁴⁺ ion that can act as a promising luminescent material [22].

Fig. 5a–e shows the excitation spectra of Ce₀.₈Sm₀.₂O₁.₉ nanoparticles prepared in EtOH/water solvent recorded at room temperature.

![Fig. 3. Raman spectra of Ce₀.₈Sm₀.₂O₁.₉ (full symbol) and undoped CeO₂ (empty symbol) solid samples prepared in i-PrOH/water solvent calcined at 700 °C.](image)

![Fig. 4. Dependence of the full width at half maximum (Γ) of CeO₂ on the calcination temperature.](image)

![Fig. 5. Excitation spectra of Ce₀.₈Sm₀.₂O₁.₉ nanoparticles synthesized in EtOH/water solvent: (a) untreated, (b) 700 °C, (c) 1100 °C and (d) 1300 °C. Inset: excitation spectrum of CeO₂.](image)
temperature (25 °C) for specimens thermally treated at 700, 1100 and 1300 °C and for the untreated material. All samples exhibit a high intensity and broad absorption band in the spectral range of 250–450 nm, assigned to the ligand-to-metal charge-transfer states O → Ce4+ (LMCT) from O2− ion to Ce4+ ion. The LMCT absorption bands are asymmetric and correlate with those of van Pieterson et al. [22] who calculated the position of O → Ce4+ LMCT absorption band of Sr2CeO4 compound using an empirical formula of optical electronegativity data given by Jørgensen [23]. However, these two absorption bands observed for the Sr2CeO4 system were related to different Ce4+-O2− distances in the lattice. The energy for a LMCT transition between the two types O2− anions and Ce4+ ion is expected at different energies.

The broad absorption bands centered at 335, 345, 370 and 370 nm in Ce0.8Sm0.2O1.9 untreated and after calcination at 700, 1100 and 1300 °C assigned to the O → Ce4+ LMCT transition are red-shifted. Besides that, the spectral profile of the bands shown in this figure is similar to that obtained for the CeO2:Sm3+ thin film [10] assigned to O → Ce4+ (LMCT) transitions [11]. The inset in Fig. 5 shows the excitation spectrum of undoped CeO2 containing two low intensity absorption bands assigned to LMCT transitions in the same spectral range observed for Ce0.8Sm0.2O1.9 samples. Moreover, the excitation spectra of Ce0.8Sm0.2O1.9 nanopowders also present the narrow bands arising from the intraconfigurational 4f–4f transitions from the 6H5/2 ground state to the following excited levels of Sm3+ ion (Fig. 5b–e) (in nm): 4D1/2 (379), 4H11/2 (394), 4I13/2 (407), 4G9/2 (429), 4I9/2 (491), 4F3/2 (530), 4G3/2 (557) and 4G5/2 (571) [24,25]. The intensities of LMCT absorption bands of nanopowder samples increase considerably compared to the narrow intraconfigurational 4f bands of Sm3+ ion with increasing the temperature of thermal treatment.

Fig. 6a–d shows the emission spectra of untreated and after calcination (at 700, 1100 and 1300 °C) of Ce0.8Sm0.2O1.9 nanopowders recorded in the spectral range of 400–750 nm. The sharp bands are characteristic of the 4G5/2 → 4H3 transitions (J = 5/2, 7/2, 9/2 and 11/2) of trivalent samarium ion. For this system, the 4G5/2 → 4H7/2 transition is dominant instead of the 4G5/2 → 4H9/2 hypersensitive transition. The ligand field interaction splits the splitting of the 4G5/2 → 4H transitions indicating that the observed maximum of Stark transitions is consistent with the Sm3+ ion in a chemical environment with distorted cubic symmetry.

The thermally treated (700, 1100 and 1300 °C) specimens exhibit broad emission bands in the 400–500 nm range with very low intensity suggesting efficient energy transfer from the O → Ce4+ (LMCT) transitions to the emitter 4G5/2 level of Sm3+ ion. In the emission spectrum of the untreated material (Fig. 6a), the O → Ce4+ (LMCT) band is observed, indicating lower efficient energy transfer than at higher temperatures. These optical data are consistent with the presence of a broad emission band recorded for the undoped CeO2 (inset in Fig. 6).

### 3.3. Density and electrical conductivity

Table 2 shows values of the relative density determined by the immersion method for Ce0.8Sm0.2O1.9 pellets sintered at 1150, 1200, 1250 and 1300 °C for 5 h. It is remarkable the high density attained at only 1150 °C for powders prepared in EtOH/water and i-PrOH/water mixed solvents. This result was explained as a consequence of the interaction among solvent, OH and water species on the surface of the nanoparticles giving rise to different degrees of particle agglomeration [13]. The strength of this interaction depends on the carbon number in the alcohol chain explaining why powders prepared in EtOH/water mixed solvent yields the highest densification.

The electrical conductivity (σ) of Ce0.8Sm0.2O1.9 pellets was determined from the usual Arrhenius expression:

$$\sigma T = \sigma_0 \exp \left( \frac{E}{kT} \right),$$

where $\sigma_0$ is the pre-exponential factor, $E$ is the apparent activation energy for conduction, $k$ is the Boltzmann constant and $T$ is the absolute temperature. Fig. 7 shows Arrhenius plots of the total electrical conductivity, $\sigma_T$, of pellets sintered at 1300 °C for 5 h prepared with specimens synthesized using different alcoholic solvents.

For specimens prepared in t-BuOH/water solvent, the total electrolyte conductivity is lower than that of specimens prepared in EtOH/water by near one order of magnitude. This difference may be attributed to the presence of pores, once the main difference between these pellets is the sintered density (Table 2). The higher total conductivity of specimens prepared in EtOH/water compared to i-PrOH/water solvents is probably due to the better impurity removal ability of that solvent during synthesis.

Therefore, taking into account the high yield and the optimized electrical conductivity of specimens prepared in EtOH/water solvent, the subsequent characterizations were carried out on pellets prepared with this nanopowder.

Fig. 8 shows the variation of the sintered density with holding time for pellets sintered at 1200, 1250 and 1300 °C. High densification occurs at 1250 and 1300 °C with short holding times. For
example, the relative density reaches 96% and 92% with only 0.1 h at 1300 and 1250 °C, respectively. A steady state of the relative density value occurs after 1 h at 1300 °C and as long as 10 h at 1200 °C. However, the sintered density is lower for decreasing the sintering temperature. These differences in sintered density influence the electrical conductivity of the Ce₀.₈Sm₀.₂O₁.₉ solid electrolyte.

Fig. 9 shows Arrhenius plots of the total electrical conductivity of Ce₀.₈Sm₀.₂O₁.₉ pellets sintered at 1200 and 1300 °C for 5 h. An increase in sintered density of less than 2.5% yielded an increase in the electrical conductivity and a decrease in the apparent activation energy from 0.90 eV (sintered at 1200 °C) to 0.86 eV (sintered at 1300 °C).

4. Conclusions

For the synthesis of SDC nanoparticles by the homogeneous precipitation method, the use of a mixture of alcohol and water as solvent allowed for reducing the filtration time by a factor of 10. The overall yield of the precipitation reaction may reach about 80% with a 70/30% (v/v) EtOH/water mixture. Values of specific surface area varied between 37 and 44 m² g⁻¹ depending on the solvent. Nanoparticles of less than 10 nm in diameter were obtained after calcination at 700 °C. The full width at half maximum of the Raman band in cerium oxide decreases linearly with the growth of the nanoparticles. The use of t-BuOH/water solvent resulted in pellets with lower sintered density and lower electrical conductivity. Powders prepared in EtOH/water solvent may attain high density (96%) with short (0.1 h) holding time at a temperature as low as 1300 °C. Excitation data of nanomaterials exhibit high intensity broad absorption band assigned to the O → Ce⁴⁺ (LMCT) transitions enveloped with the narrow absorption peaks relative to ⁶H⁵/₂ → ⁴I₄ levels of Sm³⁺ ion. On the other hand, their emission spectra show high intensity sharp peaks characteristics of the ⁴G⁵/₂ → ⁶H₂ transitions of Sm³⁺ ion and very low intensity arising from the O → Ce⁴⁺ (LMCT) transition, indicating an efficient energy transfer from the LMCT transitions to the emitter ⁴G⁵/₂ level of Sm³⁺ ion.

References