Effect of solvent on physical properties of samaria-doped ceria prepared by homogeneous precipitation

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Samaria-doped ceria solid solutions were prepared by homogeneous precipitation with hexamethylenetetramine using water and mixtures of alcohol/water as solvent. The mixed solvent influences several physical properties of the synthesized material when compared to those of samples prepared in water. The solid solution is formed, at least partially, during precipitation as demonstrated by Raman spectroscopy data. The dried precipitate is crystalline and single phase with fluorite-type structure, and consists of a mixture of anhydrous and hydrated cerium oxide with average sizes in the 5–8 nm range. Thermal decomposition of the as-synthesized material occurs at 400°C. High densification was obtained at low temperatures (∼1200°C). The electrical conductivity of grains and grain boundaries is improved for synthesized samples when compared to specimens prepared by mixing of starting oxides. These improved characteristics of synthesized powders are attributed to the interaction among the solvent and hydroxyl and water species on the surface of nanoparticles. The strength of this interaction is related to the carbon content in the alcohol chain.

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1. Introduction

Pure and rare-earth containing ceria have been extensively investigated due to their many technological applications, like mechanical polishing media, additives in ceramic processing, automobile exhaust catalyst, UV adsorbent, and solid electrolyte and electrode in solid oxide fuel cells (SOFCs)[1–5].

One of the main advantages for using doped ceria solid electrolytes instead of the well-known yttria-stabilized zirconia is the possibility of reduction of the operation temperature of SOFCs due to their higher ionic conductivity[6,7]. Samaria-doped ceria (SDC) and gadolinia-doped ceria (GDC) exhibit the highest ionic conductivity values among the rare-earth-doped cerias. Power density as high as 1 W cm−2 from anode-supported SDC fuel cells at 600°C, using humidified hydrogen as the fuel, has been reported[8].

Several efforts have been paid to the synthesis of chemically homogeneous and sinterable ceria-based solid solutions in order to improve the densification process along with reducing grain size and enhancing the ionic conductivity. The homogeneous precipitation is one of the most interesting methods to accomplish these requirements. The advantages of the homogeneous precipitation method were demonstrated by Chen and Chen[9] with the synthesis of reactive pure ceria powders, which reached full density at a temperature as low as 1250°C.

In contrast to the conventional precipitation with ammonia or oxalic acid, the homogeneous precipitation is a kinetically controlled method of synthesis, where the precipitant agent is generated in the cation solution as a result of the hydrolysis of a reagent or the combination between two reagents. This process gives rise to uniform and homogeneous distribution of the precipitant throughout the reaction medium. Urea and hexamethylenetetramine (HMT) are the most used reagents in the homogeneous precipitation giving rise to an intermediate compound in the form of hydroxide or hydrated oxide[10]. This method has also been applied for the synthesis of doped ceria solid solutions[11–13] resulting in the production of nanoparticles with less than 25 nm average size. Recently, other metal oxides have been prepared by this method, and the special features observed were attributed to the small size of the particles[14–16].

The main steps in the homogeneous precipitation method involve the mixture of the cation solution with an aqueous urea or HMT solution under stirring, and aging the resulting solution at room temperature for several hours followed by short-time aging at a temperature usually lower than 100°C. After cooling down to room temperature, the precipitate is washed and dried.
Precipitation and coprecipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening and/or agglomeration processes, which are barely isolated from each other. Moreover, these phenomena may vary according to the synthesis parameters. The addition of a low dielectric constant medium to the aqueous solution, for example, may change the kinetics of nucleation and growth of particles, which would result in changes in both the particle size and particle size distribution.

In the process of homogeneous precipitation with aqueous solution, the relative yield of the precipitation reaction has shown to increase with aging temperatures [17], and the densification has been found to be enhanced by using centrifugal casting as the conformation process [12].

In this work, samaria-doped ceria solid solutions were synthesized by a modified homogeneous precipitation method consisting in the use of different solvents as reaction medium. Physicochemical properties of powders and sintered pellets were studied in detail.

2. Experimental

2.1. Preparation methods

Cerium (III) nitrate (Ce(NO$_3$)$_3$·6H$_2$O, 99.99%, Aldrich), samarium nitrate (Sm(NO$_3$)$_3$·6H$_2$O, 99.9%, Strem Chem.) and hexamethylenetetramine ((CH$_2$)$_6$N$_4$, 99%, Alfa Aesar) were used as starting materials without further purification. Stock solutions of cerium nitrate (1.0 mol L$^{-1}$) and samarium nitrate (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). In this study three alcohols were used, including absolute ethanol (EtOH, Synth), iso-propanol (i-PrOH, Synth) and tert-butanol (t-BuOH, Synth), because of their high solubility in water. The concentration of the stock solutions was determined by complexometry. 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 cation nitrate solution, which was kept under vigorous stirring overnight at room temperature. The colloidal dispersion was maintained by the addition of a low dielectric constant medium to the aqueous solution, for example, may change the kinetics of nucleation and growth of particles, which would result in changes in both the particle size and particle size distribution.

The (CeO$_2$)$_{0.8}$(SmO$_{1.5}$)$_{0.20}$ solid solution was also prepared by the conventional mixing of starting oxides (MO) method, for comparison purposes. In this case, cerium oxide, i.e. CeO$_2$ (99.9%, Aldrich) and samarium oxide (Sm$_2$O$_3$, 99.9%, BDH) in stoichiometric proportions were mechanically mixed (T2C model, Turbula) in isopropyl alcohol with zirconia balls for 6 h. After drying, the mixture was pressed into pellets with maximum at 250 °C the weight loss of 17.29%. Therefore, it may be concluded that the precipitate consisted of a mixture of anhydrous (major constituent) and hydrated cerium oxide (minor constituent).

The X-ray diffraction patterns of SDC (20% of SmO$_{1.5}$) shown in Fig. 2 indicate that independent on the type of solvent used, the dried precipitated material is crystalline and single phase, with a cubic fluorite-type structure like that of pure CeO$_2$ (space group Fm$ar{3}$m). No diffraction peaks that could be attributed to Sm$_2$O$_3$ or other samarium compounds were detected. This result would be expected as the product of the homogeneous precipitation of cerium nitrate using HMT is, as demonstrated by thermal analyses, mostly cerium oxide, and if the precipitate is a solid solution. Crystallite sizes estimated by the Scherrer equation are 12 nm (water). Therefore, the precipitation of doped ceria in alcoholic medium favors the decrease of the crystallite size, although there was no significant difference among those values with the type of alcohol.

3. Results and discussion

3.1. Thermal and structural characterization

Some results obtained using different solvents are qualitatively similar, and thus, for the sake of brevity, only representative characterizations will be shown.

Fig. 1 shows TG and DSC curves of the dried precipitate containing 20% of SmO$_{1.5}$ prepared in i-PrOH/water mixed solvent. Three steps of weight loss may be identified in the TG curve, which are mainly related to water elimination. A small weight loss, about 1.4%, detected in the 25–150 °C temperature range, is due to loss of physisorbed water. The weight loss from 150 up to 470 °C is 3.1% and is attributed mostly to hydration water loss along with decomposition of residual organic matter. Beyond 470 °C the weight loss is negligible indicating the end of the thermal decomposition process. This temperature is considerably lower than that (~800 °C) obtained using water as solvent [13]. The reduction of the minimum temperature for decomposition completion is probably related to the interaction of alcohol molecules with H–OH or O–H groups in the precipitate. As a consequence of this interaction, a decrease in the strength of short-range adhesion forces acting on Ce–OH – HO–Ce of adjacent particles may occur. The DSC curve exhibits minor endothermic events and a broad exothermic peak with maximum at 250 °C accompanied by weight loss, which may be associated with the elimination of organic material along with residual Ce$^{3+}$ oxidation. The thermal decomposition of hydrated oxide, i.e. CeO$_2$.2H$_2$O to CeO$_2$ would result in a weight loss of 17.29%. Therefore, it may be concluded that the precipitate consisted of a mixture of anhydrous (major constituent) and hydrated cerium oxide (minor constituent).

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Fig. 3 shows Raman spectra of CeO$_2$ (i-PrOH/water) after drying and after calcination at several temperatures. An intense Raman band around 465 cm$^{-1}$ is observed in these spectra, which is attributed to a triple degenerated F$_{2g}$ active mode. This Raman
mode can be viewed as a symmetric breathing mode of the oxygen atoms around each cation [18]. Calcination of the precipitate produces a shift in the maximum amplitude of the Raman band towards higher wavenumbers, from 462.7 cm$^{-1}$ (non-calcined) to 468.3 cm$^{-1}$ (calcined at 1100 °C). Moreover, an increase in the symmetry of the Raman band along with a decrease in the full width at half maximum with increasing of the calcination temperature may be observed.

Addition of samaria to ceria produces changes in the Raman spectrum, as shown in Fig. 4. In addition to the F$_{2g}$ phonon mode, two low-intensity bands are detected at $\sim$510 and $\sim$630 cm$^{-1}$, which were correlated to the oxygen vacancies introduced as charge compensating defect [18]. It is worth noting that the Raman spectrum of non-calcined powder still exhibits these two bands. Therefore, it may be concluded that the solid solution was formed, at least partially, during the precipitation reaction. Increase of the calcination temperature leads to intensity variations in the vacancy-related Raman bands indicating minor local changes in the environment of oxygen vacancies. The maximum amplitude of the most intense Raman band occurs at 454.4 cm$^{-1}$ for non-calcined powder and gradually increases up to 460.6 cm$^{-1}$ after calcination at 1100 °C. Then, the influence of the calcination temperature on Raman spectrum is similar for pure and doped ceria and, therefore, seems to be related to higher degree of crystallinity and increase of the crystallite size. The shift of the F$_{2g}$ mode to lower frequencies in doped samples was previously observed and discussed [18]. It was shown that this effect is a consequence of dimensional changes (dilation or contraction) of the crystal lattice and of the increase in the oxygen vacancy content.

Fig. 5 shows the effect of samarium content on Raman spectra in non-calcined materials. The higher is the Sm$^{3+}$ content the higher is the contribution of the vacancy-related vibrational modes. This effect is shown in these spectra by increasing of the intensity of Raman bands in the 500–630 cm$^{-1}$ spectral range with increasing dopant content, and constitutes a further evidence of the solid solution formation during precipitation.

McBride [18] and Li [19] investigated the Raman spectra of Ce$_{1-x}$RE$_x$O$_{2-\delta}$ (RE = rare-earth ion) and observed that at high dopant contents the F$_{2g}$ mode became asymmetric. Fig. 6 shows Raman spectra for Ce$_{0.7}$Sm$_{0.3}$O$_{1.85}$ solid solution before and after calcination at several temperatures. Second-order vibrational modes in the spectral region of low wavenumbers may be seen. Increasing of the calcination temperature increases the relative intensity of the band with maximum amplitude at $\sim$257 cm$^{-1}$, and a broad band in the 300–400 cm$^{-1}$ has emerged. These second-order Raman features were observed by Weber et al. [20] in CeO$_2$ single crystals. They were identified as having primarily A$_{1g}$ symmetry and additional contributions from E$_g$ and F$_{2g}$ symmetries. In this study, these second-order Raman modes were strengthened with increasing Sm$^{3+}$ content.
Fig. 6. Raman spectra of non-calcined and calcined Ce$_{0.7}$Sm$_{0.3}$O$_{1.85}$ (i-PrOH/water).

3.2. Microstructure and densification

In the homogeneous precipitation method the precipitating agent is generated in situ and the formation of nuclei occurs thoroughly in the reaction medium, thus minimizing concentration gradients. In this case, the diffusion rate of monomer species responsible for the formation of nuclei is the same in the whole reaction volume. Then, in the absence of any external force, a sharp distribution of the nanoparticle size should be expected. Fig. 7 shows an HRTEM micrograph of the dried precipitate of Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ prepared in EtOH/water solvent. A crowded network of nanoparticles may be seen with strong faceting and well-defined edges. Most particles exhibit lattice fringes and no obvious defects or dislocations can be found in a nanoparticle. Consequently, the resulting nanoparticles are inferred to be nonporous with single crystalline structure. The hexagonal-like nanoparticles have an estimated size in the 5–8 nm range.

Fig. 8 shows SEM micrographs of SDC prepared using different solvents after calcination at 700 °C. All powders consist of spheroidal agglomerates of nanoparticles. The main difference among these powders is the state of agglomeration, which is more evident when water is the solvent (Fig. 8a).

The relative density of sintered pellets for increasing sintering temperatures is shown in Fig. 9. Sintered compacts using powders prepared in EtOH/water and i-PrOH/water solvents reached high densities at lower temperatures than powders prepared with other

Fig. 7. HRTEM micrograph of non-calcined SDC (EtOH/water).

Fig. 8. SEM micrographs of SDC powders calcined at 700 °C synthesized with different solvents: (a) water, (b) EtOH/water, (c) i-PrOH/water and (d) t-BuOH/water.
solvents and by mixing of starting oxides. It should be remarked that the densification behavior can be further improved by suitable choice of other synthesis parameters, such as the concentration of the cation solution and the aging temperature. Results shown in Fig. 9 give an idea on the role of solvent in the densification of synthesized SDC powders.

The effect produced by solvents consisting of mixtures of alcohol/water on the particle size of CeO₂ synthesized by the hydroxide precipitation was reported by Chen and Chang [21]. They explained their results considering changes in the electrostatic interaction and nucleation rate with varying the dielectric constant of the reaction medium. However, X-ray diffraction results show no significant variation of the crystallite size. Then, an additional effect predominates in this case.

The improved densification of powder compacts is mainly related to the interaction among the solvent and OH and water species on the surface of nanoparticles. One possible explanation for this effect is based on chemical interactions between OH groups of both the solvent and the precipitated material. The strength of this interaction increases with decreasing the carbon content in the alcohol chain: EtOH > i-PrOH > t-BuOH. As a consequence of this interaction, reduction in the surface-free energy of the nanoparticles occurs imparting a decrease in the number of solid bonds formed among them during the calcination step, thereby increasing the sinterability of the powder material.

The densification of pellets prepared by mixture of starting oxides is poor. The relative density increases linearly up to 1550 °C and then decreases for higher temperatures. This decrease in apparent density at high temperatures is assigned to the reduction process of Ce⁴⁺ to Ce³⁺, which is known to occur at high temperatures [7], and may be described by the following defect reaction:

\[ O_2^0 = 2O_2 + V_o + 2e^- (Ce_{Ce}) \]  

(1)

where \( V_o \) is the double ionized oxygen vacancy, \( e^- \) is an electron due to the reduction reaction and \( Ce_{Ce} \) is the reduced Ce³⁺ ion, in the Kroeger and Vink notation [22].

The difference in the densification behavior of powders prepared using water and mixed solvents can be understood taking into account the agglomeration of particles. The degree of agglomeration has been one of the main concerns in ceramic powders synthesized by solution methods. It is generally known that the so-called uncontrolled agglomeration that occurs as a consequence of the adhesion forces acting onto particle surfaces may give rise to "soft" as well as "hard" agglomerates [23]. Hard agglomerates (those which do not disintegrate during forming of compacts) in ceramic powders lead to incomplete densification and influence the grain growth rate. The formation of agglomerates is observed to occur during the synthesis of powders and during the calcination step. In general, a washing step of the precipitates in alcoholic medium is performed to prevent the formation of solid bonds among particles prepared by solution methods [24]. The present results show that this procedure is not sufficient for ceria-based ceramics, and that the use of a mixture of alcohol/water as solvent is most effective in this case.

However, the precipitated material contains alcohol residues, as revealed by the exothermic peak in the DSC curve (Fig. 1). The combustion of organic material produces heat, thus resulting in high local temperature and possible sintering of the particles, which inhibit the densification of compacts. In this context, the higher is the carbon content adsorbed onto particle surface, the higher will be the local temperature during calcination. Therefore, the use of alcohols with different number of carbons may give rise to a different degree of agglomeration after the calcination step.

The morphology of sintered materials is shown in the SEM micrographs of Fig. 10. SDC sintered at 1300 °C for 5 h exhibits good densification as can be seen in Fig. 10a (water) and b (i-PrOH/water). The main difference is the average grain size, which is lower for water/ alcohol mixed solvents. Pellets sintered at 1250 and 1150 °C show uniform morphology of small grains, but increased porosity. For an increase of 100 °C in the sintering temperature, the porosity decreases by about 5%. Additional microstructure features investigated by small-angle X-ray scattering will be published separately.

### 3.3. Electrical conductivity

Two electrolyte semicircles were recorded at 250 °C in the complex impedance plane (\( Z' (\omega) \text{ vs. } Z'' (\omega) \)) of all studied samples, as shown in Fig. 11a for sintered pellets prepared with different solvents. The high frequency semicircle (left) is due to resistive and

![Fig. 9. Dependence of the relative density on the sintering temperature.](image1)

![Fig. 10. SEM micrographs of fracture surfaces of pellets sintered at (a) 1550 °C (mixing of oxides) and (b) 1300 °C (i-PrOH/water).](image2)
Fig. 11. Impedance spectroscopy diagrams: (a) pellets prepared with powders synthesized in different mixtures of alcohol/water and sintered at 1300 °C, measuring temperature = 250 °C and (b) pellets prepared by mixing of starting oxides and sintered at 1550 °C and synthesized (i-PrOH/water) and sintered at 1300 °C.

There is a large difference in the diameter of the grain boundary semicircle of pellets prepared with t-BuOH/water solvent when compared to other samples. In general, for sintered ceramics, the grain boundaries are regions where most defects from both intrinsic and extrinsic origin are prone to be found. Taking into account the relatively low densification attained by this specimen (Fig. 9), it is reasonable to assign the large resistivity of grain boundaries also to pore contribution.

The effect of pores on electrical properties of polycrystalline ceramics has been well characterized. Depending on pore localization, inside the grains (intragranular or closed pores) or along the grain boundaries (intergranular or interconnected pores), they may change the corresponding component of the electrolyte conductivity or they may give rise to a separate semicircle in the impedance spectrum [25–27]. Whatever is the type of porosity and its concentration and size, increase of the total electrolyte resistivity occurs. Therefore, only electrical results obtained for specimens with high density will be considered.

Fig. 11b shows impedance diagrams at 250 °C obtained for pellets prepared from synthesized (i-PrOH/water) and MO powders. In these spectra, numbers over experimental points are the logarithm of the frequency, in Hz. Grain and grain boundary semicircles exhibit considerable differences in the corresponding diameter.

Fig. 12. Electrical conductivity dependence of grains (a) and grain boundaries (b) of pellets prepared with synthesized powder (i-PrOH/water, full symbol) and by mixing of oxides (MO, empty symbol).

Fig. 13. Electrical conductivity dependence of grains (a) and grain boundaries (b) of pellets prepared with synthesized powders (i-PrOH/water) and sintered at 1150, 1200 and 1300 °C.
The electrical conductivity for grains ($\sigma_g$) and grain boundaries ($\sigma_{gb}$) was calculated from the usual Arrhenius expression:

$$\sigma_{gb} = \sigma_0 \exp \left( -\frac{E_{gb}}{kT} \right)$$

(2)

where $\sigma_0$ is the pre-exponential factor, $E$ is the apparent activation energy, $k$ is the Boltzmann constant and $T$ is the absolute temperature.

Fig. 12 shows Arrhenius plots of pellets sintered at 1300 °C for 5 h (i-PrOH/water) and 1550 °C for 5 h (MO). The synthesized sample has higher grain and grain boundary conductivities, which is attributed to their relatively higher structural and microstructural homogeneities and density along with high purity. Apparent activation energy values are similar for both samples and amount $0.72 \pm 0.05$ and $0.83 \pm 0.05$ eV for grain and grain boundary, respectively.

The electrical conductivity dependence of pellets prepared with synthesized powders (i-PrOH/water) sintered at 1300, 1200 and 1150 °C (Fig. 13) does not exhibit any significant difference in the grain conductivity (Fig. 13a), as expected once the solid solution was formed during synthesis. The grain boundary conductivity (Fig. 13b) of pellets sintered at 1150 °C is slightly lower than that of other samples due to pores.

4. Conclusions

The reaction medium has a remarkable effect on surface characteristics of samaria-doped ceria nanoparticles synthesized by the homogeneous precipitation method. A maximum yield of the precipitation reaction was obtained for EtOH/water mixture. The as-prepared powder consists of a narrow distribution of crystalline SDC nanoparticles due to the use of a low dielectric constant reaction medium. Densification of compacts depends on the strength of interaction of the solvent and water and OH species on the surface of nanoparticles. The use of mixtures of alcohol/water as solvent allowed for obtaining highly sinterable SDC powders with homogeneous microstructure and improved electrical conductivity.

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