Structural investigations on yttrium - doped ceria nanopowders obtained by coprecipitation method

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The attractive properties of ceria, particularly the conductivity and chemical stability, have led to vast research efforts to investigate, characterize and develop such materials. One of the main applications of this ceramic is in the solid oxides fuel cells for intermediate temperatures IT-SOFC. The aim of this work is the preparation and characterization of cubic ceria nanopowders doped with 10 mol % yttria or Scandia. A thermal treatment (calcinations) was applied on the obtained nanopowders, which were consequently investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and selected aria electron diffraction (SAED).

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1. Introduction

Solid oxide fuel cell (SOFC) technology stands out as a potential candidate to efficiently generate cleaner sustainable energy [1–4]. However, the long-term degradation problems associated with the high-temperature operation of SOFCs (i.e., 1000 ^{0}C), and a relatively expensive manufacturing cost are still the major barriers to the widespread commercialization of this technology [3] Lowering its operating temperature to an intermediate temperature (IT) range (600–700 ^{0}C) can improve its economic efficiency, and extend its application domain to portable devices. The solid oxide electrolyte is the principal component of such IT-SOFCs. SOFCs based on the state-of-the-art yttria-stabilized zirconia's electrolyte must operate at 1000 ^{0}C to avoid unacceptable ohmic losses. Therefore, in recent years, doped ceria electrolytes have opened up the possibility for such IT-SOFCs due to their higher ionic conductivity and good thermodynamic stability in the IT range [1, 6–8]. Numerous investigations have been performed in understanding the effect of different acceptor dopants on the ionic conductivity of ceria [9–10].

Zirconia ceramics containing 10 mol% of Y_2O_3 and having a cubic structure are currently used, because have good mechanical properties and a high corrosion resistance However, at present there are two main problems with this kind of electrolyte: its low ionic conductivity at the SOFC operating temperature, and, on the other hand, its bad behavior in aging. Now, (10 mol %) [Y_2O_3 or Sc_2O_3] doped ceria electrolytes have opened up the possibility for such IT-SOFCs especially by their higher ionic conductivity and good thermodynamic stability in the (600–7000C) range. But, in parallel, the mechanical properties decrease with the increase of the doping Y_2O_3 or Sc_2O_3 quantity. To improve the mechanical properties one combines the doped ceria (matrix) with doped alumina (reinforcement) and forms the composite 10mol%Y: CeO2 + (X%)150ppmY: α - Al_2O_3. $\rightarrow$ 10YSC+(X %) 150Y: A; and, with Sc_2O_3 $\rightarrow$ 10mol % Sc: CeO_2 + (X %) 150ppmY: α - Al_2O_3. $\rightarrow$ 10ScDC+(X %) 150Y: A It is a new composite due to the introduction of the doped alumina instead of pure alumina [11, 15]

2. Experimental

2.1 The coprecipitation technique

The co-precipitation technique consists in a process of separation and deposition in solid state of two or more substances dissolved in a liquid that result in a precipitate.

To obtain CeO_2 nanopowders production, rich in yttria – (10 mol %) Y_2O_3: CeO_2 (10YSC) the crystals of $Ce(NO_3)_36H_2O$, were used along with Y_2O_3 nanopowders, distilled water and NH_4NO_3.

The preparation stages are: forming an suspension by dispersing Y_2O_3 in distilled water; preparation a $Ce(NO_3)_36H_2O$ solution in distilled water (50% volume); homogenization; mixing the Y_2O_3 suspension with $Ce(NO_3)_3$ $6H_2O$ solution; mixture homogenization by using a magnetic agitator; addition (through dropping) of NH_4NO_3 solution with distilled water (50% volume) – in excess; agitation for 3 hours (using the magnetic agitator) of the final mixture, to complete the oxide-reduction reaction; filtration under vacuum to obtain the final co-precipitate product; washing the final co-precipitate product with distilled water and ethanol, to remove the water traces; drying the final product in a drying stove for

24 h, to remove the alcohol; grinding and sieving of powder; calcinations of powder, for 2h at a temperature of 500 ^{0}C to obtain the nanopowder.

The nanopowders were isostatic pressing at 200 MPa and were obtained the 10YSC green bodies and after, the green bodies were sintered at 1550 ^{0}C for 2 h and were obtained the sintering bodies.

To obtain CeO_2 nanopowders production, rich in Scandia - (10 mol %) Sc_2O_3: CeO_2 (10ScDC), the crystals of $Ce(NO_3)_36H_2O$, were used along with Sc_2O_3 nanopowders, distilled water and NH_4NO_3 by following the same steps as in the case of doping with Y_2O_3.

Characterization of the nanopowders

The resulted nanopowder was analysed by X ray diffraction (XRD) and transmission electron microscopy (TEM) with selected aria electron diffraction (SAED), using statistical methods for interpreting results

2.2.1. XRD experimental data

The 10YSC and 10ScDC nanopowders, obtained by coprecipitation technique were investigated by XRD. The diffraction spectra (Fig. 1) for the calcined samples at 500 ^{0}C, have been measured with a Bruker-AXS D-8 series diffractometer equipped with a high-resolution silicon diode array detector (75 um/pixel). The crystalline phases where identified using the ICDD database. Their structures further analyzed using the Rietveld refinement procedure.

2.2.2. Transmission electron microscopy data

A JEOL – 200CX transmission electron microscope with the following characteristics: resolution - 0.45 nm lattice image attainable, accelerating voltage - 80 kV SEM / 200 kV TEM, magnification range 100X - 330kX, full range of sample holders, including heating, cooling and double tilt analytical, was used for structural investigations at accelerating voltage 200 kV. The YSZ (10 mol% Y_2O_3) nanopowders were applied on glass microscope lamella with 2% colloid in amyl acetate. The films were removed from the lamella substrates by immersion in distilled water, floated off on the electron microscope copper grids and were fixed with carbon thin films deposed in vacuum in a JEOL deposition installation type JEOL. For scanning electron microscopy investigations the

For scanning investigations, the sintered bodies were polished with diamond paste, after which they were covered with a Ag thin films. The SEM was made with a scanning electron microscope type HITACHI S2600N equipped with EDAX unit.

3. Results and discussion

3.1 XRD results

The X-ray powder diffraction spectra of the 500 ^{o}C calcined 10YSC and 10ScDC nanopowders (see Fig. 1) show the presence of the CeO_2 cubic phase (Fm-3m) in both compounds, and the residual Sc_2O_3 cubic phase (Ia-3) for the 10ScDC sample. The Rietveld analysis further shows that, the volume averaged crystallite size are in the order of 12-15 nm for the CeO_2 phase and 60 nm for the residual Sc_2O_3 phase. The lattice parameter values of CeO_2 for the two compounds, 5.4118 Å for 10YSC and 5.4128 Å for 10ScDC are slightly larger as compared to that of pure CeO_2 (5.4110 Å).

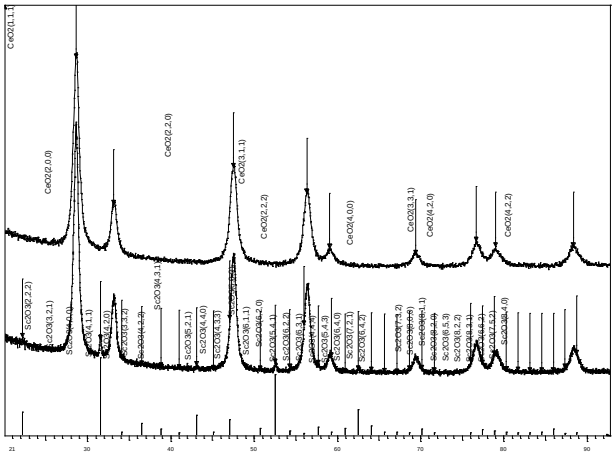

Fig. 1. X-ray diffraction spectra of 10YSC and 10ScDC nanopowders.

3.2 TEM with SAED results

The Figs. 2abcd show the transmission electron microscope images, in correlation with selected area electron diffraction patterns, for 10YSC nanopowders obtained by coprecipitation and calcined at 500 ^{0}C for 2 hours. Statistical methods were used to calculate the average diameter of the particles, the dimensional repartition of the particles and the errors. The measurements were made on approximately 1000 particles. Analyzing the transmission electron microscopy images one observes: very well-formed spherical particles, uniform, with standard deviation around the average diameter very small, well crystallized. A percentage of the particles (~ 5%) tend to form small particles with polyhedral shape, uniform.

The particles are contained in the range of dimensional values (5.8 – 15.15 nm) and the average size of the particles is $d_M = 8.11 \pm 0.052$ nm (Figs. 2abc).

Using the ICDD database for diffraction pattern, the crystalline phase – face-centered-cubic (fcc) structure of CeO_2 [ASTM 81-0792] with $a_0 = 5.4124$Å has been identified (see Fig. 2d).

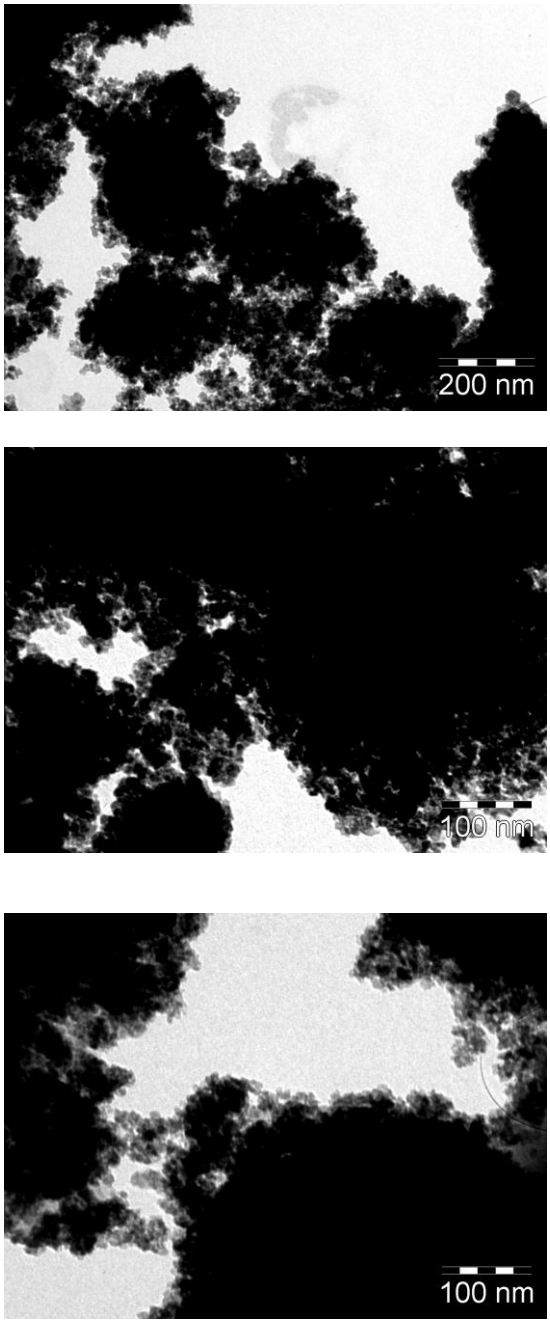

Fig. 2abcd. Transmision electron microscopy with SAED on nanopoders 10YSC.

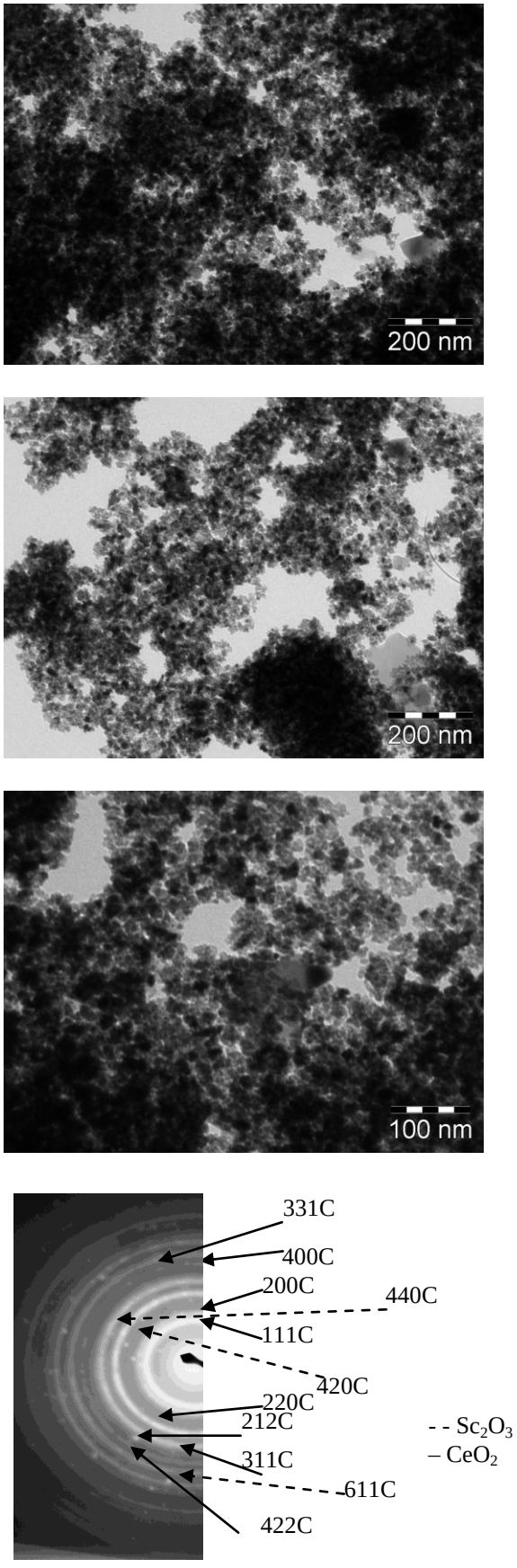

Fig. 3abcd. Transmission electron microscopy with SAED on nanopoders 10ScDC.

The Figs. 3abcd show the transmission electron microscope images, in correlation with selected area electron diffraction patterns, for 10ScDC nanopowders obtained by coprecipitation and calcined at 500 ^{0}C for 2 hours. Statistical methods were used to calculate the average diameter of the particles, the dimensional repartition of the particles and the errors. The measurements were made on approximately 1000 particles. Analyzing the transmission electron microscopy images one observes: well-formed spherical particles, uniform, with standard deviation around the average diameter very small, well crystallized. A percentage of the particles (~ 7%) tend to form small particles with polyhedral shape, uniform.

The particles are contained in the range of dimensional values (5.5 – 11.25 nm) and the average size of the particles is dM = 7.02 ± 0.039 nm (Figs. 3abc).

Using the ICDD database for diffraction pattern, the crystalline phases face-centered-cubic (fcc) structure of CeO_2 [ASTM 81-0792] with a_0 = 5.4124Å and the crystalline phases - cubic structure of Sc_2O_3 [ASTM 74–1946] have been identified (see Fig. 3d).

4. Conclusions

Yttria stabilized ceria and Scandia doped ceria nanopowders were obtained by the coprecipitation method, starting from: the crystals of $Ce(NO_3)_36H_2O$, like were used along with Y_2O_3 or Sc_2O_3 nanopowders, distilled water and NH_4NO_3. The samples were calcined at 500 ^{0}C temperature and studied by XRD and TEM with SAED.

The XRD spectra of the 10YSC and 10ScDC show that the volume averaged crystallite size of the nanopowders are in the range of 12–15 nm and that the crystal lattice is slyghtly larger compared to that of pure CeO_2. The Ce-Sc nanopwders contain cubic Sc_2O_3 residual phase with the volume averaged crystallite size of 60 nm.

The TEM with SAED made on the 10YSC samples have highlighted the following results:

- Diameter varied in the range (5.8 – 15.15nm). Mean diameter calculated using electron microscopy images and statistical interpretations is dM = 8.11 ± 0.052 nm
- The samples, calcined at 500 ^{0}C temperature have revealed only the presence of the cubic solid solution of ceria phase, revealed by SAED.
- 10YSC samples obtained by co precipitation have shown promising properties for use as electrolyte in IT – SOFC.

The TEM with SAED made on the 10ScDC samples have highlighted the following results:

- Diameter varied in the range (5.5 – 11.25nm). Mean diameter calculated using electron microscopy images and statistical interpretations is dM = 7.02 ± 0.039 nm.

The samples, calcined at 500 ^{0}C temperature have revealed: the cubic solid solution of ceria phase (> 95%) and the cubic Sc_2O_3 phase identified by SAED.

- 10ScDC samples obtained by coprecipitation have shown promising properties for use as electrolyte in IT –SOFC.

- Ceria is completely stabilized in the case of doping with yttria – sample 10YSC. In the case of doping with Scandia, ceria is stabilized but, remains a small amount of Sc_2O_3 that was not involved in the stabilization process.

- The both powders have the diameters in the dimensional range 5 – 15 nm (See TEM Results).

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