

STRUCTURAL INVESTIGATIONS OF SCANDIA - DOPED ZIRCONIA NANOPOWDERS OBTAINED BY SOL-GEL METHOD

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Scopul acestei lucrări constă în prepararea și caracterizarea nanopulberilor de zirconă cubică stabilizată cu 10 % molar de oxid de scandiu. Metoda folosită pentru prepararea nanopulberilor este sol-gel, folosind ca precursori propoxid de zirconiu și clorură/oxid de scandiu.

Nanopulberile au fost caracterizate folosind analiza termică și difracție de raze X și în consecință tratate termic la temperaturi sub 1000 °C. Pentru caracterizarea microstructurală și compozițională a nanopulberilor au fost folosite difracția de raze X, microscopia electronică de baleaj (SEM) și micriscopia electronică prin transmisie (TEM/HRTEM) cu difracție de electroni pe arie selectată (SAED). Pentru probele tratate la 700 °C, zirconia cubică este identificată ca singură fază mineralologică. Analizele MET arată dimensiuni de particule de aproximativ 10 până la 20 nm pentru probele tratate la 700 °C și 85 până la 90 nm pentru temperatură mai mare de tratament termic de 1000 °C. Forma particulelor este în principal poliedrală și prezintă o tendință scăzută de a forma aglomerate.

The aim of this work is the preparation and characterization of cubic zirconia nanopowders stabilised with 10 mol % scandia. The sol-gel method was employed for the preparation of the nanopowders, using zirconium propoxide and scandium chloride/oxide as precursors.

The nanopowders were characterised through thermal analysis and X-ray diffraction and consequently treated at temperatures under 1000 oC. X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM/HRTEM) with selected area electron diffraction (SAED) were used for compositional and microstructural characterization of nanopowders. For samples treated at 700 oC, cubic zirconia is identified as only crystallographic phase. TEM analyses showed dimensions of particles of approximately 10 to 20 nm for samples treated at 700 oC and 85 to 90 nm for higher thermal treatment temperature of 1000 oC. The shape of particles is mainly polyhedral and they present a low tendency of forming agglomerates.

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1. Introduction

Nanomaterials have unique chemical, physical, optical and mechanical properties. Because of these properties, they are useful in many domains, including sensors, catalysts, coating materials (modifiers of surface properties) and allow the miniaturization of devices.

For example, scandia stabilized zirconia (ScSZ) can be used as solid electrolyte [1]. The SOFC's working temperature is very important in what it concerns cost reduction and long-term durability. To lower the working temperature it is necessary to use an electrolyte with higher ionic conductivity. Gadolinia doped ceria, strontium oxide and magnesia doped lanthanum gallate and scandia stabilized zirconia are known as the most suitable candidates for elaborating high performance SOFC's [2]. ScSZ has been proved to have a high electrical conductivity and the highest ionic conductivity and specific conductivity [3] among zirconia doped with rare-earth ions materials. At the operating temperature of 700-1000 °C the ionic conductivity of ScSZ materials is highest at around 10 mole percent Sc_2O_3 [4].

Zirconia-based ceramics can be prepared by various methods, such as solid state reaction, co-precipitation, thermal decomposition of complex precursors and the sol-gel route [4], [5]. Among them, the sol-gel method permits the preparation of multicomponent oxide powders with superior homogeneity and small grain size. In this paper, the sol-gel method is used to obtain 10 mole % scandium stabilized zirconia nanopowders.

2. Experimental procedure

2.1. Sol Gel Preparation

The method chosen for the preparation of scandia stabilized zirconia nanopowders is the sol-gel process. The sol-gel process consists in preparing a sol, jellification the sol and then removing the solvent, followed by an appropriate thermal treatment [6]. The precursors used to prepare the scandia (10 mol %) stabilized zirconia were zirconium propoxide (FLUKA – Zirconium (IV) Propoxide Solution 70% in Propanol) and as scandium precursors were used Sc_2O_3 and ScCl_3 . The sample's composition is summarised in table 1.

Table 1.

Powder	Zirconium propoxide	Scandia	
		Sc ₂ O ₃	ScCl ₃
P ₁	X	X	
P ₂	X		X

The zirconium propoxide is characterized by a high velocity of reaction with water, thus 2-methoxy ethanol was added until a solution of 0.25 M is obtained, in order to have a better stability of the zirconia precursor. The quantities of precursors were calculated in order to obtain a molar ratio of Sc₂O₃/ZrO₂ of 1/10. The hydrolysis agent – water is also mixed with 2-methoxyethanol. Once the water is added the jellification process is starting and lasts about 30 minutes.

The gel obtained was left to mature for approximately 3 hours, and after that dried for 24 h at 110 °C. The obtained powder was thermally treated at temperatures of 700 and 1000 °C, for 2 hours.

2.2. Characterizations of the nanopowders

The powders were characterized using thermal analysis methods, X-ray diffraction (RXD), scanning electron microscopy and transmission electron microscopy (TEM) coupled with selected area electron diffraction (SAED).

The thermal differential analysis and thermogravimetry curves were obtained using a DTA-50 SHIMADZU equipment. The powder was heated up to 1000 °C, with a temperature growing rate of 10°C/minute.

X-ray diffraction data was obtained on a SHIMADZU XRD 6000 diffractometer.

The scanning electron images were obtained by using a Quanta Inspect F microscope, with a field emission gun (FEG) which has a resolution of 1.2 nm and equipped with an EDAX spectrometer with a resolution at MnK of 133 eV.

The transmission electron micrographs were obtained using a Tecnai™ G² F30 S-TWIN high resolution transmission electron microscope (HRTEM), equipped with STEM – HAADF detector, EDX and EELS, with the following characteristics: acceleration voltage of 300 KV obtained from a Shottky Field emitter with a high maximum beam current > 100nA, high probe current 0.6 nA in a 1 nm spot, 15 nA in a 10 nm spot, small energy spread 0.8 eV and with a spot drift of 1 nm / minute; TEM point resolution of 2 Å and line resolution of 1 Å.

3. Results and discussions

3.1. Thermal behaviour

The as prepared stabilised zirconia powders, obtained by the sol-gel method, were investigated by differential thermal (DTA) and thermogravimetry (TG) analysis. The DTA-TG data are shown in Fig. 1 (a, b).

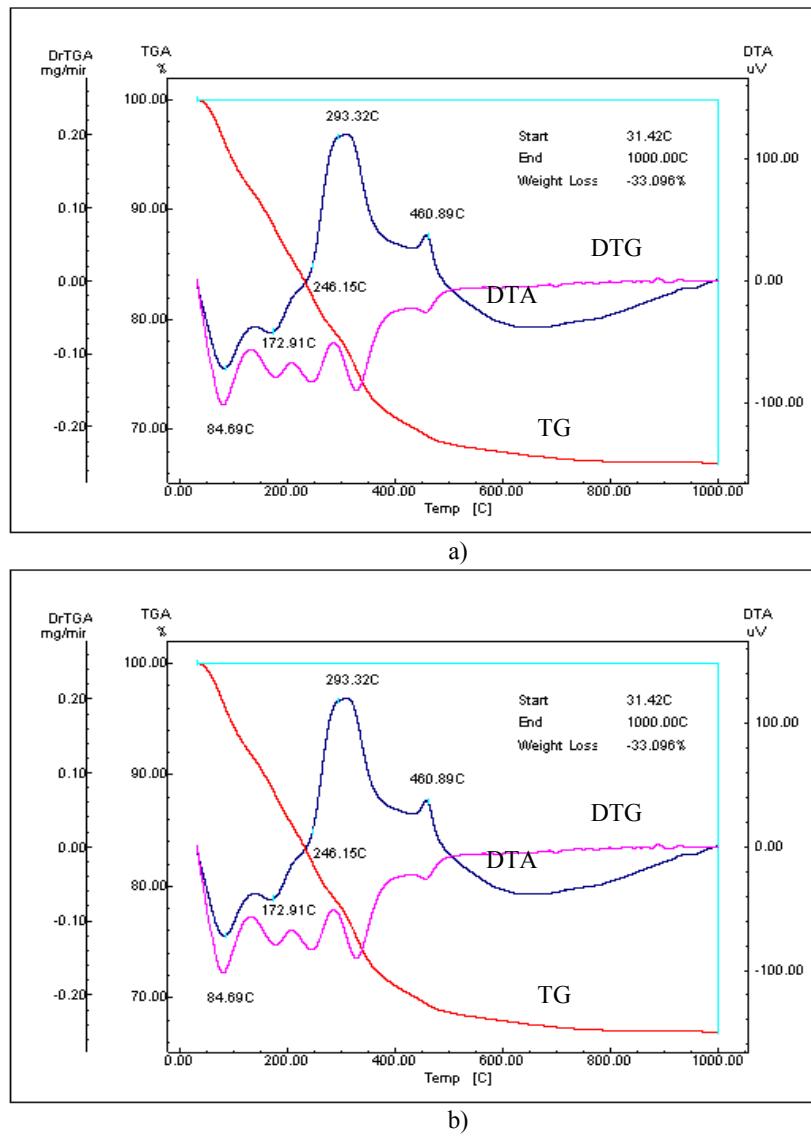


Fig. 1. Thermal analysis diagrams for P₁ (a) and P₂ (b)

The total weight loss is 23% for P_1 and 33% for P_2 . The effects between 30 °C and approximately 135 °C are due to the evaporation of the physically bonded water. The exothermal effects recorded between 135 °C and 400 °C for P_1 and 135 °C to 460 °C for P_2 can be attributed to the burning of organic residues. In the case of P_1 powder, at the temperature of 426 °C an exothermic effect is recorded, which can be attributed to a crystallization process. In the case of P_2 powder it can be also observed an exothermic effect around 460 °C that might be attributed to the burning of organic compounds, taking into consideration that is taking place with a weight loss.

By analysing these two diagrams, we can assume the fact that in the presence of Sc_2O_3 , as stabilization agent, the crystallization occurs at lower temperatures suggesting that scandium oxide has an activator role for crystallization.

3.2. Phase composition

The Sc_2O_3 (10 mol %) doped ZrO_2 powders (ScSZ), obtained through the sol – gel method, were investigated through XRD.

In Fig. 2: a, b, the XRD patterns of the synthesized P_1 and P_2 powders were plotted.

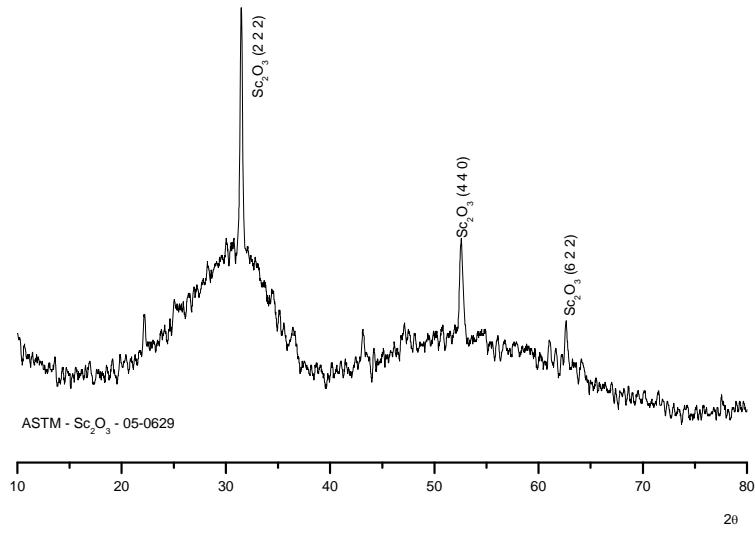


Fig. 2. a) The XRD patterns of the sol-gel synthesized precursor powders: P_1

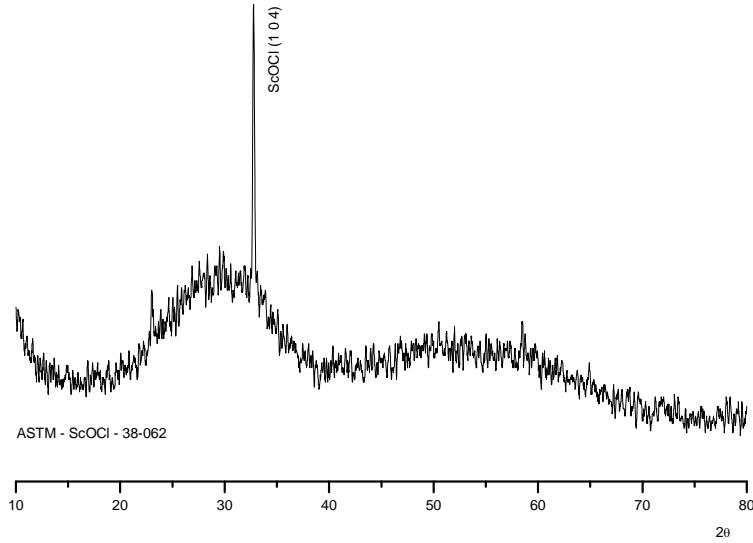


Fig. 2. b) The XRD patterns of the sol-gel synthesized precursor powders: P_2

Both XRD patterns are characterised by very broad halo diffraction peaks. In the case of P_1 peaks are present three sharp lines which can be attributed to Sc_2O_3 . In the case of P_2 pattern only one intense diffraction peak, assigned to $ScOCl$ and resulted from the hydrolysis of $ScCl_3$ was identified.

In Fig. 3. a, d, the XRD patterns of P_1 and P_2 powders thermally treated at 700 and 1000 °C for 2 hours are presented.

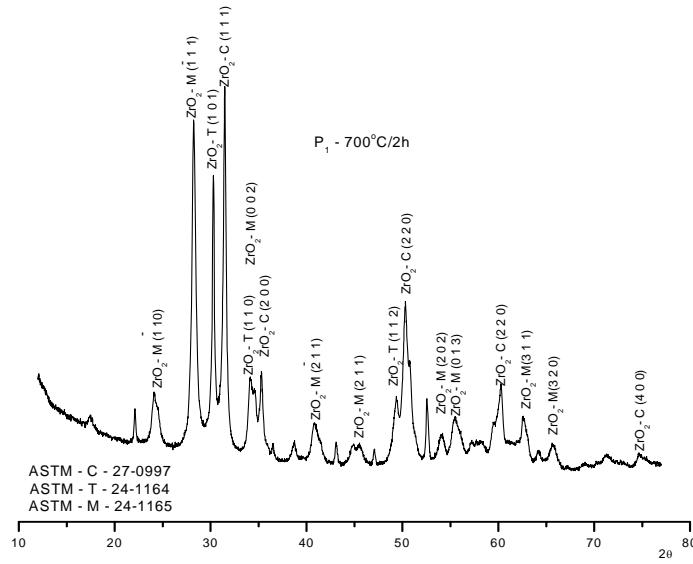


Fig. 3. a) The XRD spectra of thermally treated powders: P_1 at 700 °C

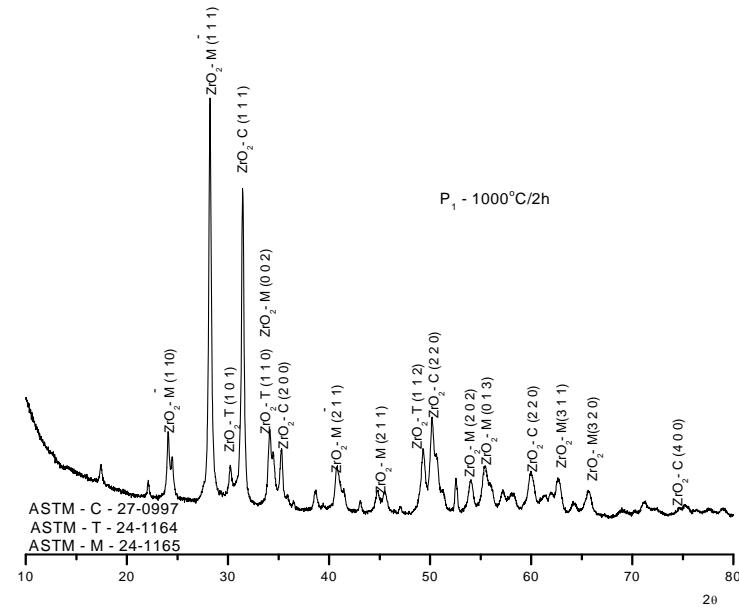


Fig. 3. b) The XRD spectra of thermally treated powders: P_1 at $1000\text{ }^{\circ}\text{C}$

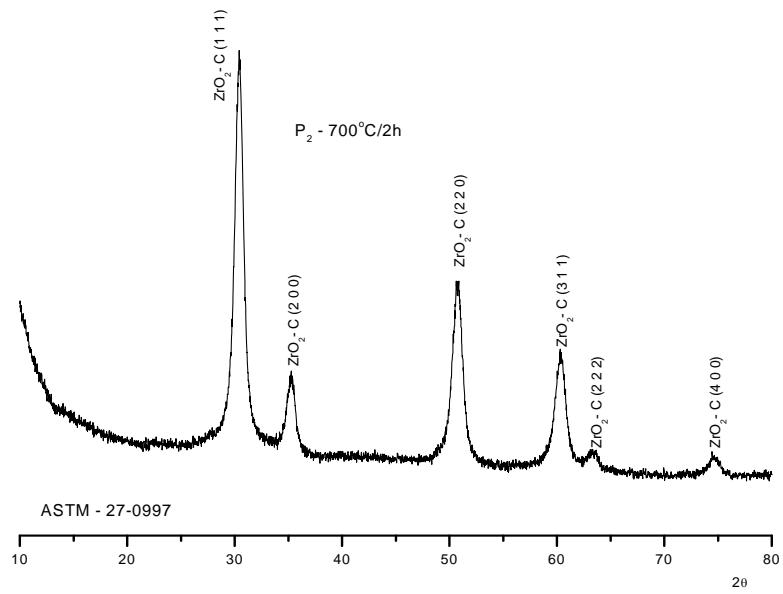


Fig. 3. c) The XRD spectra of thermally treated powders: P_2 at $700\text{ }^{\circ}\text{C}$

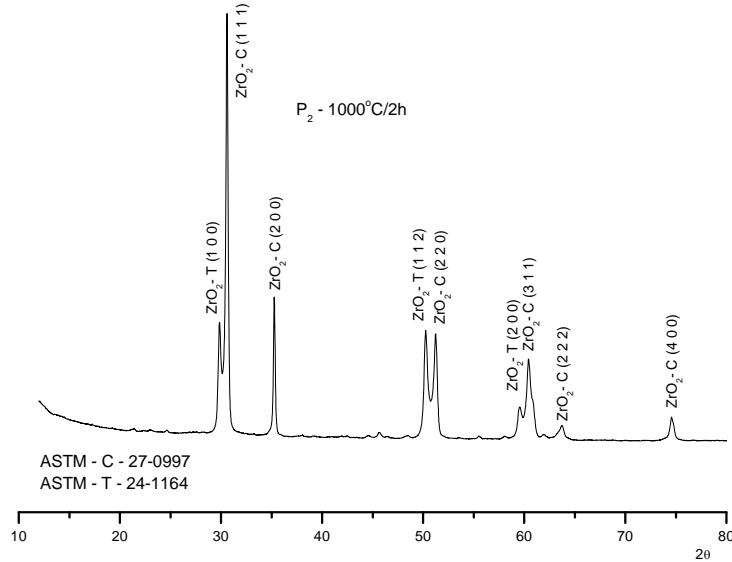


Fig. 3. d) The XRD spectra of thermally treated powders: P₂ at 1000 °C

In the case of P₁ powder all forms of zirconia are present when Sc₂O₃ is used as precursor, for 700 and 1000 °C calcination temperature.

For powder P₂, where ScCl₃ was used as precursor, at 700 °C cubic zirconia is the only phase that can be identified. At 1000 °C, also tetragonal zirconia lines are present in XRD spectrum.

It can be appreciated that ScCl₃ used as precursor for the stabilization process is much more effective as compared with the use of Sc₂O₃.

3.3. Powders morphology

In Fig. 4. a - f, are shown the SEM images of P₁ and P₂ precursors powders, and of the thermally treated powders at 700 °C and 1000 °C for 2 hours, respectively.

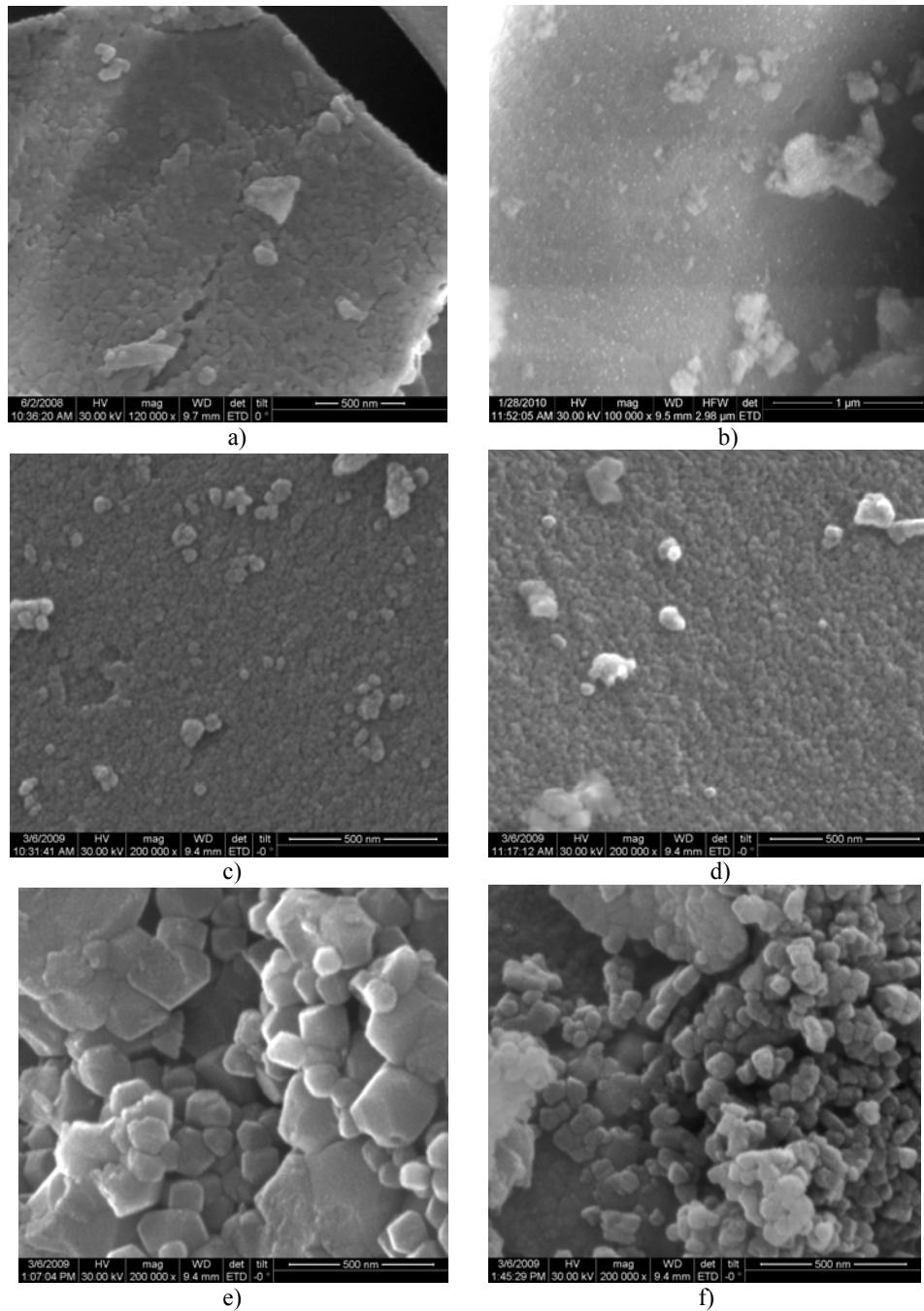


Fig. 4. SEM images of zirconia nanopowders a) P₁ as obtained, b) P₂ as obtained, c) P₁ thermally treated at 700 °C, d) P₂ thermally treated at 700 °C, e) P₁ thermally treated at 1000 °C and f) P₂ thermally treated at 1000 °C

The micrographs reveal that the powders have the tendency to form agglomerates, most probably, due to the low particle size. The as prepared powders exhibit average sizes of 25 nm (fig. 4 a) in the case of P_1 , and respectively 12 nm for P_2 (fig. 4 b).

The thermal treatment at 700 °C determines the formation of powders with mean grain size of approximately 35 nm, for both nanopowders.

At 1000 °C, the increase of the particle size is very important, the mean dimensions reaching 95 nm for P_1 (fig 4 e) and 80 nm for P_2 (fig 4 f). In the case of nanopowders P_1 the polyhedral character of grains can be clearly distinguished in fig. 4 e).

3.4. Transmission electron microscopy.

In Fig. 5. a, b are shown the TEM images with selected area diffraction patterns and high resolution images for P_1 and P_2 powders treated at 700 °C.

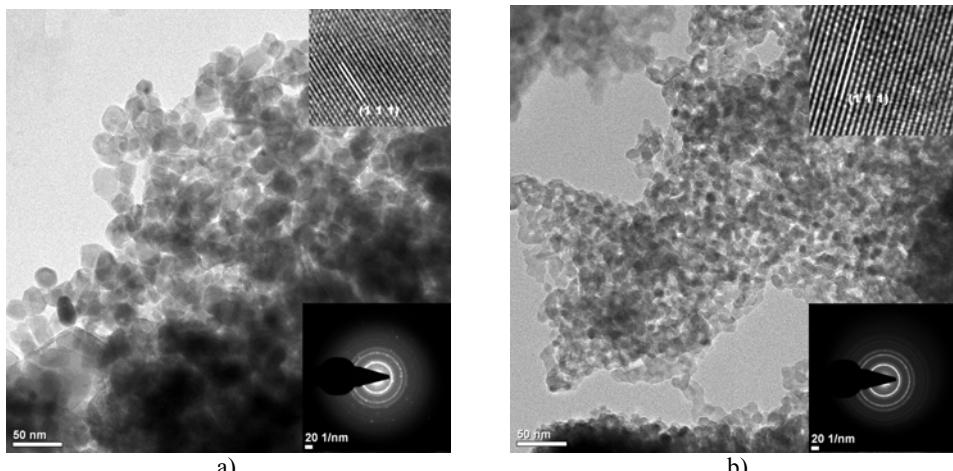


Fig. 5. TEM images obtained on treated powders at 700 °C: a) P_1 and b) P_2

The micrographs show a uniform distribution of particles, with spherical and polyhedral morphology. The mean diameter of particles is of approximately 10 nm for P_1 powder and 20 nm for P_2 .

The main crystallographic phases identified through selected area electron diffraction are monoclinic, tetragonal and cubic zirconia for P_1 and cubic for P_2 , for 700 °C thermal treatment temperature. The HRTEM image inset of zirconia nanopowder shows clearly that the distance between two atomic layers in the crystal (d) is of 2.97 Å corresponding to the (1 1 1) crystallographic plane of cubic zirconia.

In Fig. 6. a, b are shown the TEM micrographs with selected area diffraction and high resolution for powder P₁ and P₂ treated at 1000 °C.

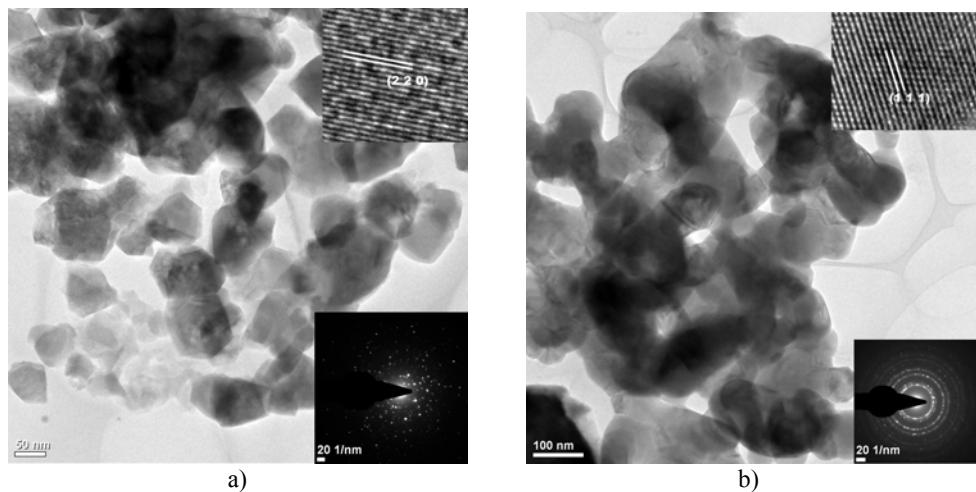


Fig. 6. TEM images obtained on treated powders at 1000 °C: a) P₁ and b) P₂

The micrographs show a uniform distribution of particles, that have mainly a polyhedral morphology for P₁ and spherical and polyhedral for P₂, with a particle size of approximately 85 nm for P₁ and 90 nm for P₂. Through selected area electron diffraction the main crystallographic phases identified are cubic, tetragonal and monoclinic zirconias for P₁ and cubic zirconia for P₂, which are in agreement with the XRD data. The HRTEM image inset of zirconia nanopowder shows clearly that the distance between two atomic layers in the crystal (d) is 1.82 Å (fig. 6 a)) and 2.97 Å (fig. 6 b)) corresponding to the (2 2 0) and (1 1 1) crystallographic planes of cubic zirconia.

4. Conclusions.

Zirconia powders can be obtained through the sol-gel method, starting from zirconium propoxid and scandium chloride/scandium oxide as precursors.

The main phases identified for P₁ powder, with Sc₂O₃ as stabiliser was monoclinic, tetragonal and cubic zirconia for both thermal treatment temperatures at 700 °C and 1000 °C. For P₂ powder, with ScCl₃ as precursor for scandia stabiliser, treated at 700 °C, cubic zirconia is the only phase identified and for the powder treated at 1000 °C tetragonal zirconia can also be identified.

The microstructural analyses carried out through SEM and TEM reveal that both P₁ and P₂ powders have a tendency to form agglomerates and exhibit polyhedral and spherical morphology, respectively. The mean sizes of all nanopowders were under 100 nm. The grain size increase, as expected, with the

thermal treatment temperature. SAED investigations are in agreement with XRD data.

We may conclude that the 10 mole % scandia-stabilized zirconia nanopowders prepared by the sol-gel method are showing promising characteristics for application in the IT-SOFC electrolyte.

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