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Thermal Evolution and Stability of Pr₂O₃-doped ZrO₂ Powder and Thin Films

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Abstract

ZrO₂ powders and films with 5, 8, 9 and 10 mol % of Pr₂O₃ were prepared by a modified sol-gel method using liquid precursors. The thermal stability of the different phases is crucial in order to use this material in devices such as fuel cells, where the appearance of unwanted spurious phases causes a negative impact in the efficiency of such devices. DTA-TG and HT-XRD analysis carried out on the powders show that crystallization takes place around 500 °C. Heat treatments over 1000 °C produces destabilization of the initial crystallization cubic phase in the powders as well as in the films. However, aging treatments consisting in thermal cycles between room temperature and 750 °C, which is the temperature of technological interest, do not affect the structure, the microstructure and the stresses state of the Pr-doped ZrO₂ thin films.

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1. Introduction

Praseodymium belongs to the lanthanide group and has an ionic radius of 126.6 pm (Pr⁺³, 8-fold coordination). The Pr⁺³/Zr⁺⁴ ionic radius ratio is such that $(r_{Pr^{+3}}/r_{Zr^{+4}}) \sim 0.29$, which limits the solubility of the

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Pr^{+3} in the ZrO_2 lattice, according to Hume-Rothery's empirical rules. The use of Pr as an additive to stabilize the tetragonal or cubic phases of zirconia has been studied mainly in powder or sintered samples. The formation of a solid solution of Pr on Zr was confirmed on powders with Pr content up to 15 mol % synthesized by coprecipitation and it was found that higher concentrations of Praseodymium correspond to higher crystallization temperatures and a higher percentage of stabilized ZrO_2 (Bonamartini Corradi et al., 2001). Similar results were obtained on powders with lower concentrations, such as 0.53 at % of Pr (Ramos Britos et al., 2006) and 1.5 and 2.5% of Pr_2O_3 (Isasi-Marin et al., 2006). Available information of crystal structure and its thermal evolution in films of Pr_2O_3 doped ZrO_2 is yet limited, in particular within the range of concentrations of Pr of interest for solid oxide fuel cells (SOFC). SOFC is an electrochemical energy converter which directly converts the chemical energy of a fuel gas into electrical energy. Due to the high power density of SOFC systems compared to other fuel-cell types, many researches are in progress to develop micro-SOFCs for use in small, portable electronics which are mostly based on the thin film technology. For this application, it is necessary to have a thin film ceramic electrolyte, dense and structurally stable in the range of temperatures of operation of micro-SOFC, between 400 °C and 650 °C. The PrO_x - ZrO_2 system has been studied in thin films synthesized by dip-coating but for concentrations starting from 25 mol % of PrO_x to be potentially applied in oxygen storage devices (Narula et al., 1999). The aim of this paper is to study the effects of the Pr^{+3} in the zirconia crystal structure and its thermal evolution on thin films and powders. Four concentrations of this system were analyzed: 5, 8, 9 and 10 mol % of Pr_2O_3 .

2. Experimental

Samples were prepared by Chemical Solution Deposition (CSD). The spin-coating technique was used to deposit the films onto alumina substrates. The precursor solution was prepared by mixing Zirconium n-propoxide, Praseodymium nitrate and Acetoin into 1-propanol as a chemical chelating. Four solutions were prepared to obtain films with 5, 8, 9 and 10 mol % of Pr_2O_3 . Film coatings of about 0.5 μm were deposited by the multilayer process (five to eight layers) onto alumina and Platinum substrates. Each layer was heat treated at 500 °C for 0.5 h in normal atmosphere. Powders were obtained by low vacuum (4 kPa) solvent evaporation of the solutions and drying (200 °C for 1 h). X-Ray Spectra were performed by using a Philips X'Pert Pro Diffractometer. Films were analyzed at RT after annealing at increasing temperatures. Powders were also analyzed at increasing temperatures, by an *in situ* experiment, using a heating chamber Anton Paar HTK10. Rietveld refinement was performed by MAUD software (Luterotti et al., 1999). The surface morphology was studied by atomic force microscopy, using a Nanotec Electronica AFM. Thermal cycling treatments in temperature range RT- 750 °C for 24 hs each were performed to study stability of the metastable phase present at 750 °C. By means of a DTG-60H Shimadzu analyzer, simultaneous Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA) measurements were carried out on the as-obtained powder gels from room temperature to 800 °C in normal atmosphere. Alumina crucibles and an α -alumina reference were used.

3. Results

3.1 Thin Films

The crystallization (fluorite-type cubic phase Fm-3m) starts between 500 °C and 600 °C in films (600 nm) deposited onto alumina. The onset of crystallization increases for increasing Pr_2O_3 content. For temperatures lesser than 1000 °C, the crystal structure remains unchanged regardless the Pr content. Figure 1A shows GI-XRD spectra at RT of the 8 mol % Pr_2O_3 - ZrO_2 film (deposited on Pt) after annealing at 750 °C that exhibits diffractions corresponding to the cubic phase.

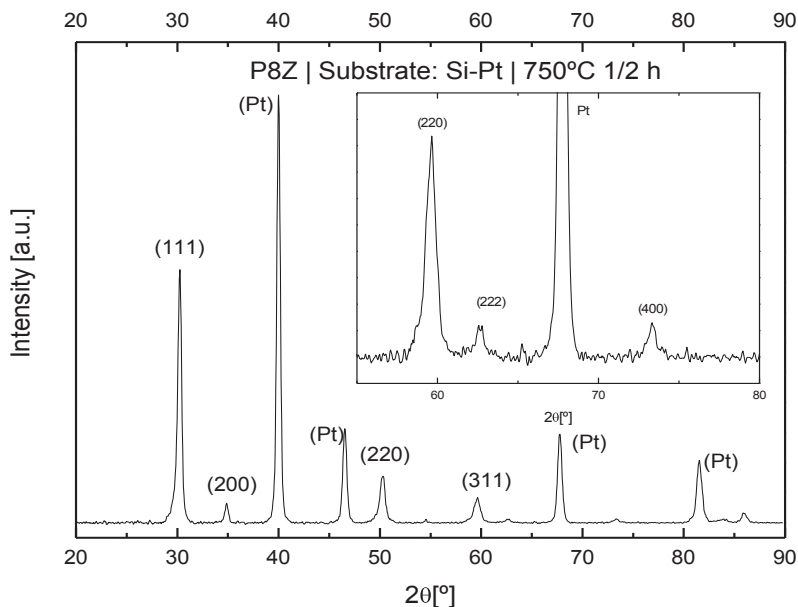


Fig. 1. X-ray diffraction pattern of 8 mol % $\text{Pr}_2\text{O}_3 - \text{ZrO}_2$ thin film after annealing at 750 °C and detail of the high-angle zone.

Table 1. Cell Parameter a (nm) of $\text{Pr}_2\text{O}_3 - \text{ZrO}_2$ thin films between 600 °C and 1000 °C.

5% Pr_2O_3	8% Pr_2O_3	9% Pr_2O_3	10% Pr_2O_3
0.5117 (2)	0.5169 (2)	0.5175 (2)	0.5182 (2)

In addition to the $c\text{-ZrO}_2$, the presence of monoclinic zirconia $m\text{-ZrO}_2$ (with symmetry $P2_1/c$) is observed in the films with 5% Pr_2O_3 heat treated at 1100 °C, which results from the partial destabilization of cubic zirconia $c\text{-ZrO}_2$ (Table 2). In contrast, in films with 8, 9 and 10% of Pr_2O_3 the monoclinic phase appears only when they were heat treated at temperatures higher than 1200 °C. For samples annealed at 1200 °C, the monoclinic fraction increases at increasing Pr content; on the other hand, the relation is reversed for the films annealed at 1300 °C. This unexpected result could be related to the fact that at 1300 °C the Pr solubility increases in the structure of the high temperature zirconia phase, which is partially retained after cooling at RT.

Table 2. Phases distribution after different heat treatment temperatures.

Temp. [°C]	5% Pr_2O_3		8% Pr_2O_3		9% Pr_2O_3		10% Pr_2O_3	
	c (%)	m (%)	c (%)	m (%)	c (%)	m (%)	c (%)	m (%)
1100	73	27	100	0	100	0	100	0
1200	8	92	66	34	58	42	43	57
1300	11	89	16	84	20	80	25	75

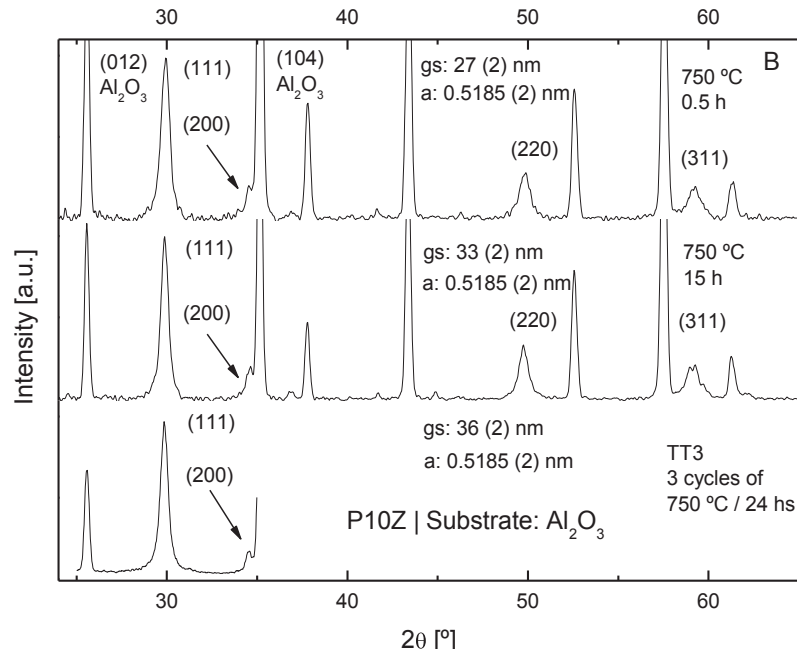


Fig. 2. X-ray diffraction patterns of 10 mol% Pr_2O_3 as sintered (0.5 h) and after ageing thermal treatments.

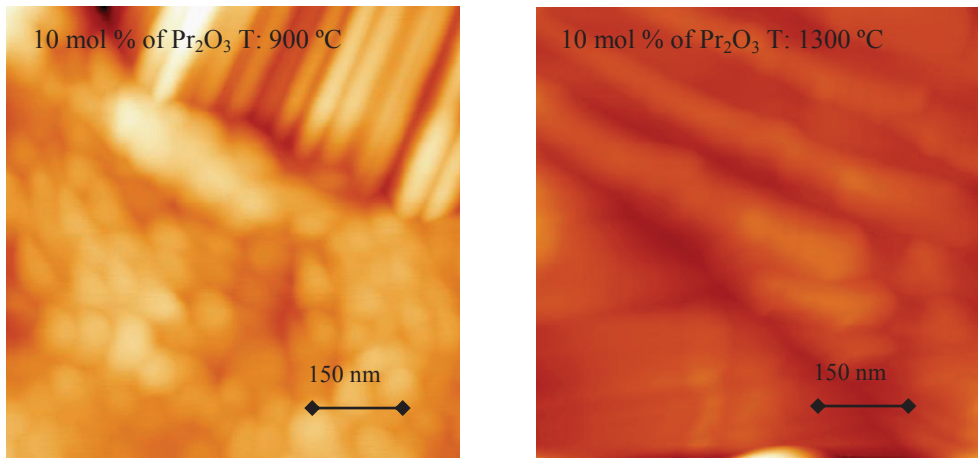


Fig. 3. AFM surface image from film with 10% of Pr_2O_3 treated at 900 °C and 1300 °C.

In order to study the stability of the zirconia metastable phase obtained at low temperature, 10 mol % $\text{Pr}_2\text{O}_3\text{-ZrO}_2$ deposited on alumina and treated at 750 °C were exposed to ageing heat treatments, consisting in thermal cycles between RT and 750 °C. Figure 2 shows GI-XRD spectra of the specimens treated at different times. Relative intensity, shape and position of diffraction peaks remain unaltered after aging. Therefore, the structure, the cell parameters and the residual stresses have not been changed. This result indicates that these films could be built in devices that operate at temperatures of 750 °C without degradation.

By taking random regions of different sizes on the surface of the samples, AFM images of the films show two well differentiated structures on their surface (Fig. 3): grains that we can assume spherical and elongated or columnar structures, which can be observed from 900 °C heat treatment temperature. They are probably due to the activation of twin systems that often occur during the phase change from tetragonal to monoclinic (Morales and Rühle, 2006; Simha, 1996).

3.2 Powders

In situ XRD by means of a heating chamber (HT-XRD) of powder with 5, 8, and 10 mol% of Pr₂O₃ shows that crystallization has started below 500 °C. The incipient crystalline structure emerging from amorphous phase is a tetragonal / cubic structure. For 10 mol% of Praseodymium oxide, at 500 °C, the diffractions peaks of the t/c structure are less defined, indicating a delay in the crystallization in respect of the lowest concentrations. Up to 1000 °C, crystallization continues and maintains the initial t/c structure. The Pr seems completely incorporated into the ZrO₂ network as the cell parameters grow to increasing concentrations of dopant (0.5195 nm, 0.5215 nm, 0.5230 nm for 5%, 8% and 10% of Pr₂O₃ respectively, at 1000 °C).

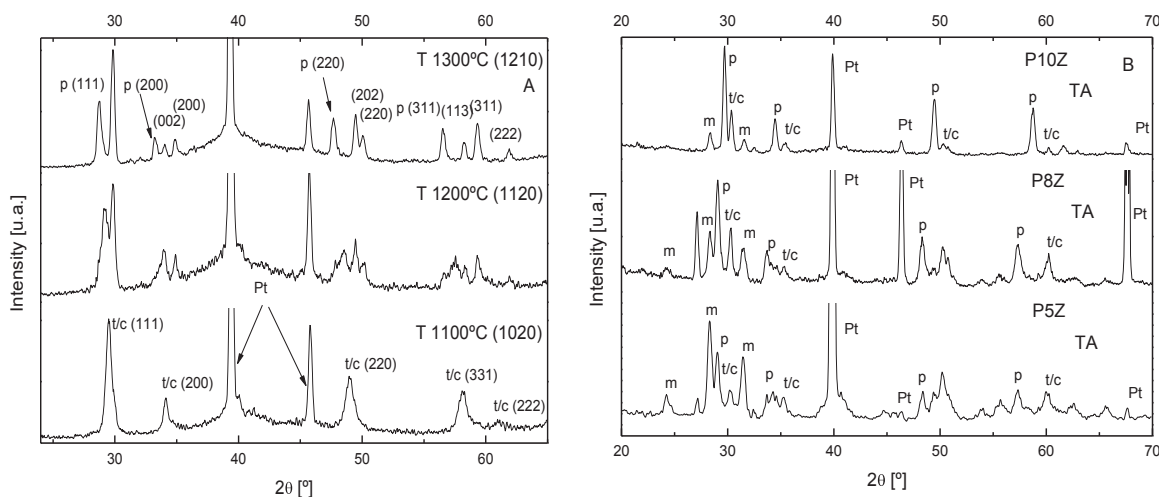


Fig. 4. A. *In situ* X ray diffraction patterns of the three highest temperatures for P10Z. B. Room temperature X ray diffraction patterns for powders after 30 min (calcination) at 1300 °C.

From 1000 °C, XRD analysis shows peaks corresponding to a tetragonal structure, being this specially evident for lower concentrations of Pr₂O₃ while a second cubic phase with pyrochloic structure (Pd-3m) appears early at higher concentrations of dopant oxide. At room temperature, after treatment, there are three resulting phases in the powders: a monoclinic phase (m), a tetragonal / cubic (t/c) phase attributed to stabilized ZrO₂ and pyrochloic (p) phase rich in praseodymium, whose main diffractions are indicated in Figure 4B. This second cubic phase, segregated from tetragonal ZrO₂, is due to the supersaturation of praseodymium caused by its poor solubility because of the large ionic radius difference between the two cations. After segregation, the tetragonal phase with a low concentration of Pr (lower than 1 mol %) decomposes partially into the monoclinic phase during cooling. As a result, at room temperature, there are three phases: a pyrochloic phase rich in praseodymium, metastable tetragonal zirconia and monoclinic zirconia. The amount of the t/c - Zr phase does practically not vary with the content of praseodymium. The

percentage of monoclinic structure decreases almost linearly with concentration and consequently, the pyrochloric phase is increased (Table 3).

Table 3. Phases coexistence in powders of $\text{Pr}_2\text{O}_3\text{-ZrO}_2$ obtained with *in situ* XRD experiments.

Temp. [°C]	P5Z			P8Z			P10Z		
	p (Pr)	t/c (Zr)	m (Zr)	p (Pr)	t/c (Zr)	m (Zr)	p (Pr)	t/c (Zr)	m (Zr)
1200	0.07	0.93	-	0.05	0.95	-	0.39	0.61	-
1300	0.22	0.78	-	0.22	0.78	-	0.49	0.51	-
RTA	0.23	0.16	0.61	0.47	0.15	0.38	0.58	0.18	0.24

DTA-TG analysis show several exothermic peaks and related masses losses at temperatures lower than 500 °C. These peaks correspond to the decomposition and burning of organic (465 °C) waste and are overlapped with the onset of crystallization (500 °C). At higher temperatures, only a low intensity peak centered in 700 °C is observed. This peak, associated with a small mass gain, is attributed to the removal of residual oxygen vacancies arising during the synthesis process (Caruso et al. 1997). Above 150 °C and up to 500 °C, the thermogravimetric analysis of the powders of the four concentrations of Pr_2O_3 studied show a loss of continuous mass, with a total value close to 50% of the initial mass corresponding to the elimination of the organic waste of the synthesis process. On cooling, neither significant changes in mass, nor endothermic or exothermic peaks were observed.

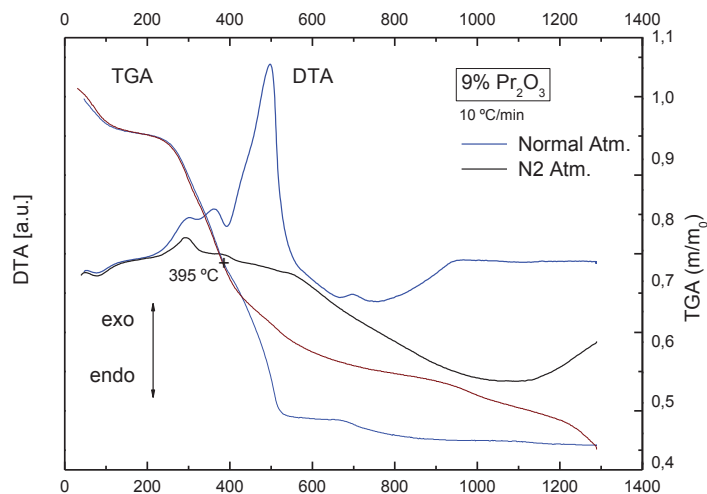


Fig.5. DTA/TG diagrams of samples with 9 mol % of Pr_2O_3 under Nitrogen (red), and normal (blue) atmosphere.

Powders with 5% and 9% of Pr oxide content were analyzed under atmosphere of N_2 and air by DTA / TG (Figure 5). DTA / TG under nitrogen atmosphere does not show a strongly exothermic reaction around 450 °C which can be seen in other measurements under normal atmosphere, which is attributed to the burning of the organic groups and crystallization. Despite this, XRD analysis performed on the material residue of the DTA / TG studies (Figure 6) shows a good crystallization, regardless of the treatment atmosphere. The mass change

on the two atmospheres is almost the same up to a temperature close to 400 °C, where the removal rate becomes smaller in the case of N₂ atmosphere and the two TG curves begin to separate.

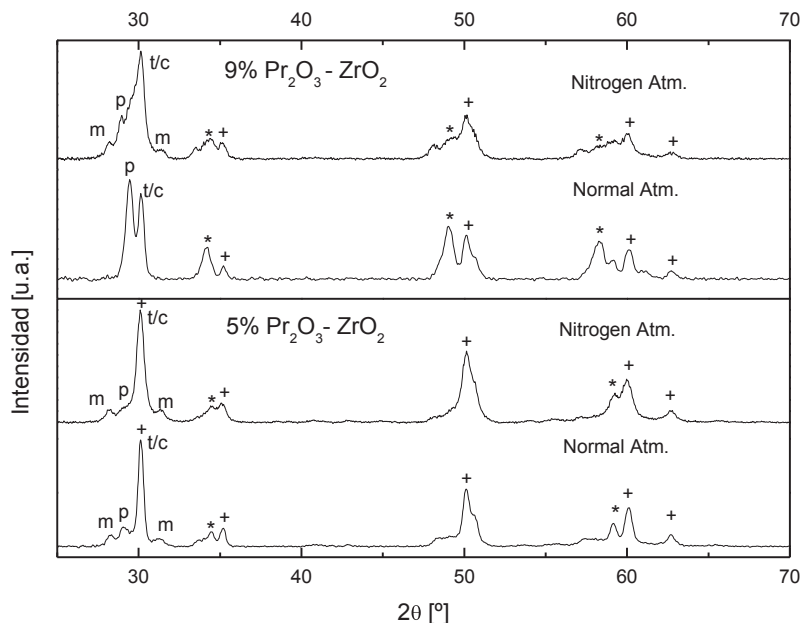


Fig.6. Diffraction pattern for 5 and 9 mol % of Praseodymium oxide of powders residue of the DTA / TG studies. Phases are indicated on the main diffraction peaks and the rest of them are noted by += t/c; x= m; *= p.

At the end of the DTA/TG test, the total weight losses are very similar both in N₂ and in the air (see Fig. 4). XRD can distinguish three different structures in the powders of 5 and 9 mol % of Pr₂O₃ obtained after performing the DTA/TG characterization: a tetragonal / cubic phase which is attributed to stabilized ZrO₂, a monoclinic phase and a pyrochloric phase (Pr₂Zr₂O₇) (Fig.6). Under nitrogen, the sample with a higher content of praseodymium (P9Z) has a greater fraction of the cubic phase rich in Pr while the incidence of t/c-ZrO₂ and m-ZrO₂ phases has been reduced approximately by 35% regarding the amounts of these phases in the P5Z.

In normal atmosphere, the powder with a concentration of 9 mol % of Pr₂O₃ shows no appreciable quantities of monoclinic structure, which is observed in a 17% in the powder with 5 mol % of Pr oxide. A higher content of Pr seems to involve a higher content of pyrochloric phase, which is detrimental to the tetragonal and monoclinic phases, as in samples treated under nitrogen atmosphere.

Table 4. Percentage of phase distribution of powders residue of DTA/TG experiment, obtained by XRD.

Atm.	P5Z			P9Z		
	t /c (Zr)	m (Zr)	p (Pr)	t/c (Zr)	m (Zr)	p (Pr)
N ₂	0.60	0.20	0.20	0.38	0.13	0.49
Air	0.55	0.17	0.28	0.42	-	0.58

4. Conclusions

Pr₂O₃-ZrO₂ thin films and powders were obtained from solutions using Zr n-propoxide, Pr nitrate, acetoin and n-propanol as starting materials, chelating agent and solvent, respectively. The presence of Pr⁺³ in the network of ZrO₂ stabilizes the tetragonal / cubic phase up to 1000 °C both in films and in powders, and the films exhibit the activation of a twinning system. The phase evolution in the material is influenced by a constraint effect of the substrate on the film. A pyrochloric cubic phase appeared in the powder at temperatures over 1000 °C. However this phase is absent in the films during all the thermal treatment. The onset of crystallization depends on the oxygen content of the atmosphere used during the burning of the organic residual, the normal atmosphere allows crystallization at temperatures below 500 °C. Aging treatments that consist in thermal cycles between room temperature and 750 °C, which is the temperature of technological interest, do not affect the structure, the microstructure and the stresses state of the Pr-doped ZrO₂ thin films. Therefore, thin films of Pr doped ZrO₂ could be applied as solid electrolyte in micro-SOFCs operating at intermediate temperature.

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