METASTABLE TETRAGONAL PHASE IN NANOCRYSTALLINE ZrO_2-CeO_2 POWDERS

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Abstract

The aim of this work was to study the stability of the tetragonal phase in nanocrystalline ZrO_2 - 2 to 15 mol% CeO2 powders, synthesized by a nitrate-glycine gel-combustion process. Phases present in these materials were analyzed by X-ray diffraction and Raman spectroscopy. The average crystallite sizes of all the powders were in the range 8-14 nm. Fully tetragonal materials were obtained for a CeO_2 content of 5 mol% or higher. By analyzing powders treated at different temperatures, it was established that tetragonal phase is more stable for higher CeO_2 contents and for smaller crystallite size. For the ZrO_2-15 mol% CeO_2 powder, it was found that very high specific surface areas can be reached by reducing the calcination temperature, without increasing the amount of carbonaceous residues.

Resumen

En este trabajo se estudió la estabilidad de la fase tetragonal en polvos nanocristalinos de ZrO_2 - 2 a 15 %molar de CeO_2 sintetizados por el método de gelificación-combustión con nitrato-glicina. Las fases presentes en estos materiales fueron analizadas por difracción de rayos X y por espectroscopía Raman. El tamaño medio de cristalita fue de 8 a 14 nm para todos los polvos analizados. Se obtuvieron materiales completamente tetragonales para contenidos de CeO_2 de 5 %molar o mayores. Estudiando polvos tratados a distintas temperaturas, se comprobó que la fase tetragonal es más estable con contenidos de CeO_2 crecientes y tamaños de cristalita menores. En el caso del polvo de composición ZrO_2-15 %molar CeO_2, se encontró que es posible alcanzar muy altas áreas específicas reduciendo la temperatura de calcinación, sin aumentar apreciablemente el contenido de residuos carbonosos.

Introduction

Although ZrO_2-based ceramics are very attractive materials from a technological point of view due to their excellent electrical and mechanical properties, the basic properties of these materials are still under investigation. One important subject of study is the mechanism for the retention of the tetragonal phase at room temperature in powders and ceramics, since it is not fully understood yet.

Pure ZrO_2 exhibits three polymorphs, which have monoclinic, tetragonal and cubic symmetries. The monoclinic phase is stable at room temperature and transforms to the tetragonal phase at 1170°C. At 2370°C, the tetragonal phase transforms to the cubic one. Both transformations are martensitic in nature and reversible on cooling, although the $t \rightarrow m$ transformation occurs at a lower temperature (about 950°C). The cubic phase exhibits the fluorite (CaF_2) structure (*Fm3m* space group), while the tetragonal and monoclinic ones exhibit the same structure but slightly distorted. The tetragonal phase belongs to the $P4_2/nmc$ space group and its crystal structure can be easily derived from the fluorite structure of the cubic phase by elongating one of the three equal crystallographic axes of the cubic structure and displacing the oxygen ions from their ideal positions of this phase along the same axis.

The high temperature tetragonal and cubic phases can be retained at lower temperatures by doping with other metal oxides such as Y_2O_3, CaO, CeO_2, etc. However, the tetragonal phase is not stable at room temperature, being the monoclinic phase the stable one. It has been established that the tetragonal phase can be retained in dense ceramic specimens provided the grain size is smaller than a critical value (of about 1 μm) and these materials, called 'Tetragonal Zirconia Polycrystals' (TZP), have been extensively investigated [1-2]. TZP ceramics exhibit exceptional strength and toughness and they are also employed as a solid electrolyte for moderate temperature electrical devices. However, they present low temperature degradation in moist environments (the tetragonal phase transforms to the stable monoclinic one) constituting a very important obstacle to their full exploitation [1-2]. The conditions required to retain the tetragonal phase in the case of powders are not clearly understood yet. However, it is well known that a crystallite size of about 10-20 nm is essential. Although it is believed that the surface free energy plays a very important role for the stabilization mechanism [3], stresses and defects could also be relevant [2]. Literature scarcely reports research on this topic, being most of it based on the study of crystallite size and microstrains by X-ray line profile analysis [4].

The aim of the present work was to study the stability of the tetragonal phase in nanocrystalline ZrO_2-2 to 15 mol% CeO_2 powders synthesized by a nitrate-glycine gel-combustion route. Gel-combustion methods are based on the gelling and subsequent combustion of an aqueous solution containing salts of the desired metals (usually nitrates) and some organic fuel, such as glycine, citric acid, urea, etc. [5-6]. The combustion process is due to the exothermal redox reaction between nitrate ions and the fuel. The large volume of gases produced during this reaction promotes the disintegration of the precursor gel yielding nanoparticles.

Experimental procedure

Powder synthesis:

Nanocrystalline ZrO_2-X mol% CeO_2 powders (X = 2, 5, 8, 10, 12 and 15) were synthesised by a nitrate-glycine gel-combustion process [6]. $ZrOCl_2.8H_2O$ and $Ce(NO_3)_3.6H_2O$ were dissolved in an excess of nitric acid in a ratio corresponding to the desired final composition. The nitrate solution was concentrated to a low volume by

thermal evaporation in order to eliminate chlorine. Glycine in a proportion of 5 moles per mole of metal atom was added and the pH of the solution was adjusted to pH = 3-4 with ammonium hydroxide. This solution was concentrated on a hot plate until a black gel was obtained, which finally burned due to a vigorous exothermic reaction. Resulting powders were calcined at 600°C in air for 2 hours in order to eliminate the carbonaceous residues. The system remained homogeneous during the whole process and no precipitation was observed. In the case of the composition of ZrO_2-15 mol% CeO_2, powders calcined at 350°C were also studied. All the chemicals used for this synthesis were of analytical reagent grade.

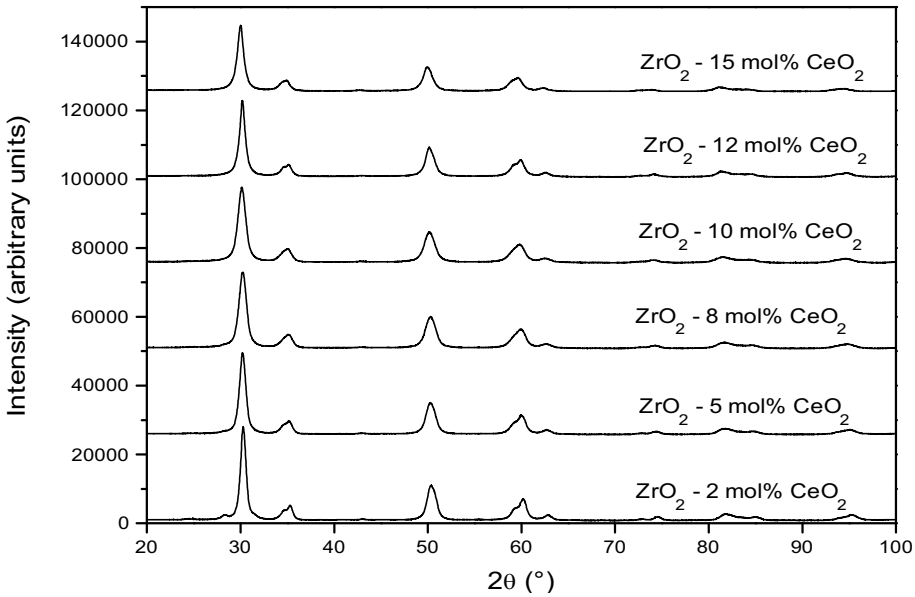

***Figure 1**: Diffractograms of ZrO_2-CeO_2 powders.*

Structural characterization:

Qualitative and quantitative analyses of all the powders were performed by X-ray diffraction (XRD) and Raman spectroscopy.

XRD analysis was carried out using a PW 3710 Philips diffractometer operated at 40 kV and 30 mA with Cu-Kα radiation and a graphite monochromator. Data in the angular region of 2θ = 20-100° were collected in a step-scanning mode, with a step length of 0.02°. The low-angle region of 2θ = 27-33° was carefully studied in order to observe the most intense reflections of the monoclinic phase and its concentration was determined by means of the Toraya method [7]. The crystallite size of the powders was determined by the Scherrer equation [8]. For the structural study of fully tetragonal powders, the Rietveld analysis program FullProf.98 (v. 0.2, Laboratoire Leon Brillouin) was employed. The *$P4_2/nmc$* space group was assumed with (Zr^{4+},Ce^{4+}) cations and O^{2-} anions in 2a and 4d positions, respectively. The cell parameters, *a* and *c*, and the fractional *z* coordinate of the O^{2-} anion in the tetragonal asymmetric unit, *z(O)*, were refined. These structural parameters will be given in terms of the usual pseudo-fluorite cell [1]. The peak shape was assumed to be a pseudo-Voigt function. The background of

each profile was adjusted by a six-parameter polynomial function in $(2\theta)^n$, n = 0-5 and isotropic atomic thermal parameters were used.

Raman spectra were recorded using a DILOR XY multichannel spectrometer equipped with a CCD detector. The 514.53 nm excitation line of an argon ion laser was used. All experiments were carried out using a laser power of 20 mW in macroscopic back-scattering geometry. Position and half width of half maximum (HWHM) of Raman bands were obtained by decomposition into Lorentzian-shaped peaks with PeakFit software (v. 4.0, Jandel Scientific). The monoclinic content was determined using the procedure proposed by Alzyab *et al.* [9].

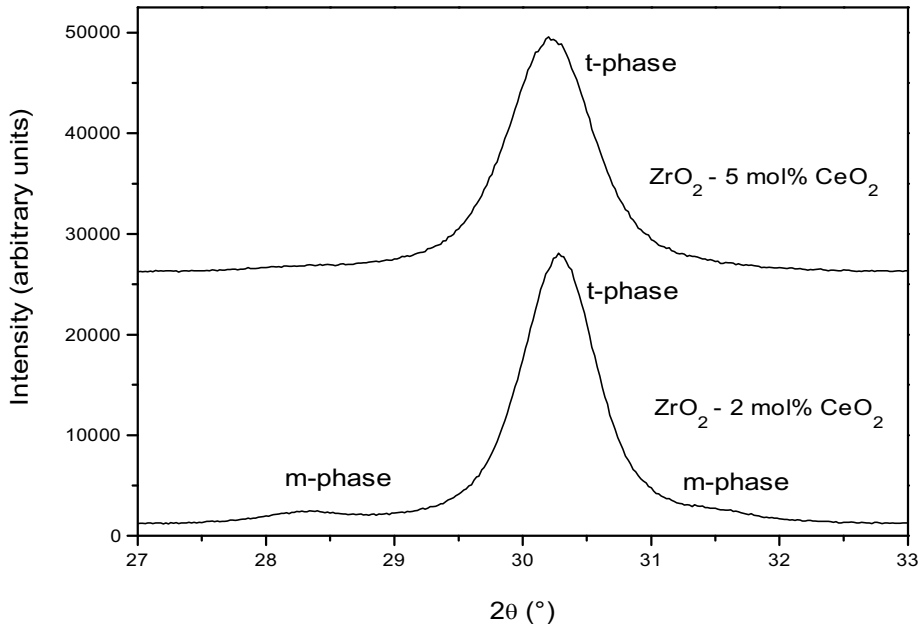

Figure 2: *Low-angle region of the diffractograms of the ZrO_2-2 and 5 mol% CeO_2 powders.*

Morphological characterization:

The morphology of all the powders was studied by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) employing Philips 505 and Philips CM200 microscopes, respectively. The compositional homogeneity was verified by means of energy dispersive spectroscopy (EDS) with an EDAX 9900 microprobe. The specific surface area of ZrO_2-15 mol% CeO_2 powders was measured with a Quantachrome Autosorb-1-C analyzer using the multipoint Brunauer, Emmett, and Teller (BET) adsorption technique. The carbon content of ZrO_2-15 mol% CeO_2 powders was determined with a LECO CS-200 carbon and sulfur analyzer.

Results and discussion

Figure 1 shows the diffractograms of the nanocrystalline ZrO_2-CeO_2 powders, which clearly exhibit the tetragonal phase as the main one. Figure 2 shows the low-angle

region of the ZrO_2-2 and 5 mol% CeO_2 powders. The ZrO_2-2 mol% CeO_2 powder exhibits a small monoclinic content, which resulted of about 6 mol% as determined by the Toraya method. Differently, the ZrO_2-5 mol% CeO_2 powder only presents the (111) reflection of the tetragonal phase. Powders with higher CeO_2 content were also fully tetragonal materials. The average crystallite sizes of all the powders are listed in Table 1.

XRD data of fully tetragonal powders were analyzed by means of Rietveld refinements. Table 2 summarizes the resulting structural data. It can be observed that the axial ratio *c*/*a* decreases with increasing CeO_2 content, as Figure 3 shows. This behavior is usual for ZrO_2-based ceramics [10]. The z-coordinate of the oxygen ions *z(O)* remains almost constant, as it is exposed in Table 2.

Table 1. *Crystallite sizes of ZrO_2-CeO_2 powders synthesized by a nitrate-glycine gel-combustion process, calcined at 600°C, evaluated by Scherrer equation.*

POWDER	Crystallite size (nm)
ZrO_2-2 mol% CeO_2	14 ± 1
ZrO_2-5 mol% CeO_2	12 ± 1
ZrO_2-8 mol% CeO_2	9.5 ± 0.5
ZrO_2-10 mol% CeO_2	9.0 ± 0.5
ZrO_2-12 mol% CeO_2	8.0 ± 0.5
ZrO_2-15 mol% CeO_2	8.0 ± 0.5

Table 2: *Structural parameters of fully tetragonal nanocrystalline ZrO_2-CeO_2 powders, calcined at 600°C, obtained by Rietveld refinements. Standard Rietveld agreement factors (R_p, R_{wp} and R_{exp}) are also shown.*

CeO_2 content (mol%)	*a* (Å)	*c* (Å)	*c/a*	*z(O)**	R_p	R_{wp}	R_{exp}
5	5.1057 (4)	5.1997 (4)	1.0184 (2)	0.197 (1)	5.67	6.33	3.96
8	5.1232 (5)	5.2123 (5)	1.0174 (2)	0.198 (1)	5.47	6.22	3.77
10	5.1247 (5)	5.2122 (5)	1.0171 (2)	0.198 (1)	4.83	5.70	3.74
12	5.1308 (5)	5.2113 (5)	1.0157 (2)	0.196 (1)	5.29	5.98	4.32
15	5.1414 (5)	5.2162 (5)	1.0146 (2)	0.196 (1)	5.36	6.09	4.41

**Fractional z coordinate of the O^{2-} anion in the tetragonal asymmetric unit. This anion is in the (1/4,1/4,z) position. The value of z is 1/4 for the cubic phase.*

Figure 4 shows the Raman spectra of the ZrO_2-CeO_2 powders. Only the ZrO_2-2 mol% CeO_2 powder exhibits the 179 and 189 nm^{-1} bands corresponding to the monoclinic phase, while the others only present the six Raman active modes of the tetragonal phase, confirming the qualitative analysis performed by XRD. By means of

the procedure of Alzyab *et al.* [9], a monoclinic content of 3.6 mol% was obtained for the ZrO_2-2 mol% CeO_2 powder.

In order to evaluate the influence of the crystallite size, powders calcined at 1200°C were also studied. XRD data showed that these materials presented crystallite sizes in the range of 30-50 nm and a high monoclinic concentration (>70 mol%) was found for powders with CeO_2 content lower than 10 mol%. These results indicate that the tetragonal phase is more stable for high CeO_2 content and smaller crystallite size. Critical crystallite size to retain the tetragonal phase is about 30-40 nm for ZrO_2-5 to 8 mol% CeO_2 powders and increases with increasing CeO_2 content.

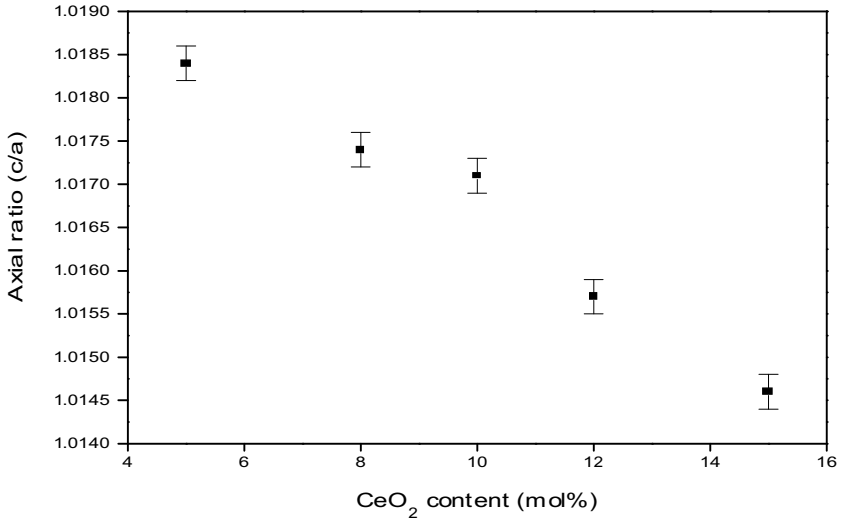

Figure 3: *Variation of the axial ratio (c/a) with the CeO_2 content.*

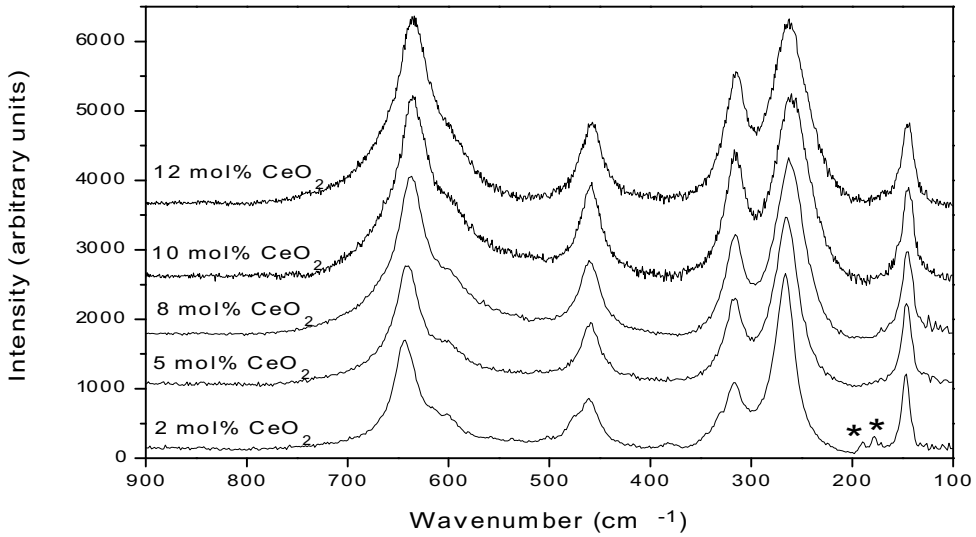

Figure 4: *Raman spectra of ZrO_2-CeO_2 powders (* indicates monoclinic bands).*

The powder morphology was similar for all the compositions studied in this work. Powders were formed by large porous aggregates, with typical sizes of 20-50 μm. The pores were produced by the fast expulsion of gases during the combustion process. TEM observations with higher magnification showed that these aggregates were constituted by weakly agglomerated, spherical nanoparticles. It is worth to remark that the spherical shape of the nanoparticles is typical of powders synthesized by the gel-combustion process, and it has been found for other materials [11,12]. EDS study confirmed the compositional homogeneity of the all the powders. The specific surface area of ZrO_2-15 mol% CeO_2 powders calcined at 600°C was of (11.2 ± 0.1) m^2/g.

The influence of the calcination temperature on powder morphology was studied for ZrO_2-15 mol% CeO_2 powders. Since the specific surface area was relatively low for powders calcined at 600°C, materials calcined at lower temperatures were analyzed. It was found that a crystallite size of (5.9 ± 0.3) nm and a specific surface area of (93 ± 2) m^2/g can be obtained by calcination at 350°C. The carbon content was measured for ZrO_2-15 mol% CeO_2 powders calcined at 350 and 600°C and it resulted of (0.10 ± 0.01) wt.% for both materials. This is an important result, since it confirms that the calcination temperature can be reduced in order to get a higher specific surface area and a smaller crystallite size without causing a large increase in the carbon content.

It is interesting to compare different methods for the synthesis of ZrO_2-CeO_2 nanopowders. Several wet-chemical methods have been reported, such as hydrothermal synthesis [13], high-energy mechanical milling [14], polymerized complex method [15,16], coprecipitation [17,18], sol-gel [18] and forced cohydrolysis [19]. Papers reported in the literature demonstrated that high-energy mechanical-milling [14] and coprecipatation [17,18] do not allow the synthesis of single-phase powders in the whole compositional range. Mechanical milling produces multiphase materials even for long milling times, probably due to compositional inhomogeneity of the samples [3]. This problem is even worst in the case of the coprecipitation method, since it leads to a mixture of tetragonal ZrO_2 and cubic CeO_2, independently of the calcination temperature (up to 900°C) In contrast, hydrothermal synthesis [13], polymerised complex method [15,16], sol-gel [18] and forced cohydrolysis [19] seem to produce compositionally homogeneous materials. Gel-combustion methods also yield very homogeneous powders, since it is based on the rapid combustion of homogeneous gels. Regarding to the powder morphology of ZrO_2-rich materials synthesised by different routes, it is worth to mention that the specific surface area reported in the present paper for ZrO_2-15 mol% CeO_2 powders calcined at 350°C (93 m^2/g) is one of the highest values reported in the literature.

Conclusions

The stability of tetragonal phase in ZrO_2-2 to 15 mol% CeO_2 powders has been investigated. It was found that this metastable phase can be retained for nanocrystalline powders with a crystallite size range: 8-15 nm for 5 mol% CeO_2 content or higher. It was proved that the tetragonal phase is more stable for higher CeO_2 content and smaller crystallite size. In addition, it was established that very high specific surface areas can be

obtained by means of calcination at relatively low temperature (350°C) without increasing the amount of carbonaceous residues.

Acknowledgements

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