

Nanostructured Spark Plasma Sintered Ce-TZP Ceramics

Sylvia A. Cruz,[‡] Rosalía Poyato,^{‡,†} Francisco L. Cumbrera,[§] and Jose A. Odriozola[‡]

[‡]Instituto de Ciencia de Materiales de Sevilla, Universidad de Sevilla-CSIC, Avda, Américo Vespucio 49, 41092 Sevilla, Spain

[§]Departamento Física de la Materia Condensada, Universidad de Sevilla, 41080 Sevilla, Spain

In this work, spark plasma sintering (SPS) of 10 mol% CeO₂doped ZrO₂ nanocrystalline powders, obtained by a two-step synthesis procedure, allows the preparation of fully densified nanostructured ceramics. The CeO₂-ZrO₂ powders with particle size below 100 nm are obtained after CeO₂ deposition on hydrothermally synthesized ZrO₂ particles by the impregnation method.Tetragonal CeO₂-ZrO₂ ceramics are obtained when sintering at 1200°C without holding time. A graded material containing tetragonal, monoclinic, and pyrochlore phases are obtained when sintering at 1200°C and for 5 min holding time. This is explained in terms of the gradual reduction of Ce^{4+} to Ce³⁺ species by carbon in the graphite environment during SPS. With the successful combination of the stabilizer coating technique and SPS, we achieve not only the stabilization of the tetragonal phase in the ceramics, but also good control of the grain size, by producing nanostructured ceramics with 40-70 nm grain sizes.

I. Introduction

T ETRAGONAL zirconia polycrystalline (TZP) ceramics have excellent mechanical properties and attractive ionic conductivity, which allows their use in very different fields, such as structural applications, fuel cell technologies, gas sensors, or solid-state electrolytes.^{1–7} Enhancements of electrochemical properties,⁴ and mechanical properties, such as plasticity,⁵ wear resistance,⁶ and fracture toughness,⁷ have been reported for doped-ZrO₂ ceramics when decreasing the grain size.

In the last years, increasing attention has been paid to CeO₂-doped zirconia, due to its excellent hydrothermal stability, which makes it an interesting material to be used as catalyst,^{8,9} and remarkably high transformation toughness, which makes it of considerable interest for advanced structural applications.^{10,11} In addition, an enhancement of mechanical properties when decreasing grain size has been reported for this material. Wang *et al.*¹¹ have reported that both the fracture strength and fracture toughness increase when decreasing grain size from 15 to 2 μ m, for the composition containing 12% CeO₂. However, despite the expected enhancement in mechanical properties for nanostructured CeO₂–ZrO₂ ceramics, the published studies are scarce.^{12,13}

The properties of sintered ceramics are highly dependent on the initial powder properties as well-demonstrated in literature. Conventional synthesis routes, such as solid-state, ball milling, sol-gel, combustion, or co-precipitation, have been the most widely applied methods for the preparation of CeO_2 -ZrO₂ solid solution nanocrystalline powders. Recently, nonconventional methods, such as microwave-induced combustion or suspension drying, have been reported, with advantages as simple processing and equipment.^{14,15} The processing of very fine-grained, even nanostructured, ceramics requires, besides the use of nanometric polycrystalline powders, the use of sintering techniques that allow densification while retaining grain size. To overcome the problem of grain growth, unconventional sintering and densification techniques have been proposed. These include the use of grain growth inhibitors¹⁶ or high-pressure densification.^{17,18} However, although the nanometric grain size is achieved, secondary phases can be developed in the ceramic in the former case, and extreme pressures as high as 8 GPa are needed in the latter. The spark plasma sintering (SPS) method has emerged as an effective technique for the processing of fully densified nanostructured materials. In this technique, the simultaneous application of pressure and electrical current through the sample during heating allows fast densification of ceramics at relatively low temperatures and pressures.¹⁹⁻²¹

In the last few years, few attempts of processing CeO_2 -ZrO₂ solid solution or related systems by means of SPS have been carried out.^{16,22,23} The main problem of SPS on Ce-TZP is the susceptibility to reduction of CeO₂ to Ce₂O₃ in vacuum or low oxygen partial pressure atmospheres, which has an effect on the stability of the tetragonal zirconia phase at room temperature. During SPS, a strongly reducing atmosphere is created around the powder by the graphite die and punches. Different studies have shown the catastrophic degradation and cracking of samples when sintering in hot pressing or graphite furnace.^{22–25} Huang *et al.* have reported the formation of macrocracks in 12 mol% CeO₂–ZrO₂ ceramics prepared by spark plasma sintering of commercial co-precipitated powder at 1450°C for 2 min.²³

Xu et al. have reported the partial retention of tetragonal phase in 8 mol% CeO₂-doped ZrO₂, spark plasma sintered at 1300°C without holding time. Besides the t-ZrO₂ phase, a 66 vol% monoclinic phase and a trace amount of a Zr–Ce–O cubic solid solution were found.²² However, the nanostructure was not achieved in this study. A graded microstructure has been reported in tetragonal $1 \mod \% Y_2O_3 + 6 \mod \%$ CeO₂-co-doped ZrO₂ with 2 wt% Al₂O₃ as sintering additive, spark plasma sintered at 1450°C for 2 min,17,23 with grain sizes of 0.44 μ m in the core and 0.17 μ m in the edge of the ceramic. This microstructural gradient, together with the increased t-ZrO₂ phase transformability found in the ceramic, has been related to the partial reduction of CeO₂ to Ce₂O₃ during sintering. When sintering at 1550°C, elongated grains with CeAl₁₁O₁₈ composition have been observed in the surface region. The presence of this phase has been related to the reduction of CeO₂ to Ce₂O₃, as it is only found in the more reduced edge layer.

In the present study, nearly fully densified nanostructured 10 mol% CeO₂-stabilized tetragonal ZrO_2 was processed by means of a combination of a two-step powder synthesis route and SPS. The effects of the SPS sintering conditions on the phase composition and microstructure of the ceramics were investigated. The formation of a graded microstructure and a pyrochlore phase was discussed and was related to the CeO₂ reduction.

H.-E. Kim-contributing editor

Manuscript No. 29718. Received May 11, 2011; approved October 29, 2011. † Author to whom correspondence should be addressed. e-mail: rosalia.poyato@icmse.csic.es.

II. Experimental Procedure

(1) Powder Synthesis and Characterization

A quantity of 10 mol% CeO₂-stabilized ZrO₂ powder was obtained by a two-step synthesis procedure. In a first step, a hydrothermal route was followed to synthesize nanocrystalline ZrO₂ powder. Zirconyl nitrate hydrate (ZrO (NO_3) ·xH₂O, 0.5 M) and sodium hydroxide (NaOH, 0.5 M) were mixed together and sonicated for 30 min. Later, 10 mL of the solution was disposed in the hydrothermal vessel with 2 mL of ethanol, closed and heated in a furnace for 5 h at 200°C. When the vessel achieved room temperature, the solid was washed with distilled water and dried at 100°C for 1 h. In a second step, cerium oxide was deposited onto the ZrO₂ particles by the impregnation method. The adequate amount of 1 M Ce(NO)₃·6H₂O solution was added to the solid to obtain a 10 mol% CeO₂-ZrO₂ powder, the resulting slurry was then dried for 12 h at 100°C. Finally, the ceramic powder was calcined at 700°C for 4 h.

X-ray diffraction (PANalytical X'Pert Pro diffractometer, Almelo, the Netherlands) was used for phase identification of the powders. Diffraction patterns were recorded using CuK α radiation over a 2θ range of 10–90° and a position-sensitive detector using a step size of 0.05 and a counting time of 1 s per step.

The cerium and zirconium contents of the samples were determined by X-ray fluorescence spectrometry (XRF-Panalytical AXIOS PW4400, Almelo, the Netherlands) sequential spectrophotometer with a rhodium tube as the source of radiation.

The BET-specific surface areas were measured by nitrogen adsorption at liquid nitrogen temperature (Micromeritics ASAP 2000, Atlanta, GA). Before analysis, the samples were degassed for 2 h at 150°C in vacuum.

(2) Ceramics Processing and Characterization

The SPS (Model 515S; SPS Dr Sinter Inc., Kanagawa, Japan) of the ceramic powder was performed in vacuum in a 15-mm diameter cylindrical graphite die/punch setup, under a uniaxial pressure of 50 MPa at 1200°C for 5 min, or without holding time. The heating rate was 100°C/min. Temperature was measured using a thermocouple, which was placed in a bore hole in the middle part of the graphite die. The sintered ceramics of ~15 mm in diameter and ~2 mm in thickness were polished to eliminate the surface carbon. Density of the ceramics was determined using the Archimedes' method, using water as the immersion liquid.

Powder X-ray diffractometry is perhaps the most useful method for the quantitative analysis of the phases present in multicomponent ceramics. However, the determination of accurate compositions is sometimes difficult because of significant overlap of Bragg reflections, as well as possible texture effects. For this reason, results obtained using traditional quantitative XRD methods generally are unsatisfactory. To approach phase identification and Rietveld quantitative analysis on the sintered ceramics, diffraction patterns were recorded using a step size of 0.02 and a counting time of 10 s per step on the polished cross-sectioned surfaces of the ceramics. The profile refinements were performed using the Rietveld program FULLPROF.²⁶ This code is derived from a classical Rietveld program (DBW3.2S). In this work, the peak shape was assumed to be a pseudo-Voigt function and the refinement included the following aspects: (i) the background, which was modeled as a third-order polynomial function; (ii) the scale factors; (iii) the global instrumental parameters (zero-point 2θ shift and systematic shifts, depending on transparency and off-centering of the sample); (iv) the lattice parameters for all phases; and (v) the profile parameters [Caglioti halfwidth parameters and the mixing parameter (h) of the pseudo-Voigt function]. This refinement was performed first

without any texture correction. Subsequently, the texture correction was included using the March–Dollase function.²⁷

Raman spectra were recorded on fracture surfaces using a dispersive microscope (Horiba Jobin Yvon LabRam HR800, Kyoto, Japan), with a 20-mW He-Ne green laser (532.14 nm), without filter, and with a 600 g/mm grating. The microscope used a $50 \times$ objective and a confocal pinhole of 100 μ m. The Raman spectrometer was calibrated using a silicon wafer.

Microstructural investigation was performed by scanning electron microscopy (Hitachi S4800 SEM-FEG, Tokyo, Japan).

III Results

The XRD patterns for hydrothermally synthesized ZrO_2 and calcined CeO₂-coated ZrO₂ powder are presented in Fig. 1. It is clear, the presence of crystalline monoclinic ZrO₂ phase (JCPDS 01-078-0047) in the starting powder, and the tetragonal solid solution (JCPDS 01-080-0) accompanied by the m-ZrO₂ phase in the CeO₂-coated ZrO₂ powder. This is in agreement with the phase diagram reported by Kaspar *et al.* for ZrO₂–CeO₂ solid solution.²⁸

According to Balducci *et al.*^{29,30} the energetics of the reduction of cerium cations is reduced on increasing the amount of zirconium ions present in the solid solution. In our case, 10 mol% CeO₂–ZrO₂, the reduction potential of the Ce⁴⁺/Ce³⁺ system reduces from 7.5 to 6.1 eV. Moreover, in the synthesis process, the zirconia nanoparticles are obtained by hydrothermal treatment in ethanol, which is further partially eliminated by drying in air at 200°C. This treatment results in the presence of adsorbed alcoxide species that upon ceria addition and further calcination may also favor the reduction of Ce³⁺ result in an easiest diffusion of the cerium cation into the ZrO₂ matrix, which occurs at fairly low temperatures.

The textural properties of ZrO_2 and calcined CeO₂-coated ZrO_2 powders are summarized in Table I. The chemical composition of the latter, obtained by XRF, was 10 mol% Ce and 90 mol% Zr.

The SEM micrographs of the hydrothermally synthesized ZrO_2 powder and the calcined CeO_2 -coated ZrO_2 powder are shown in Fig. 2. The ZrO_2 powder shows an ellipsoidal shape [Fig 2(a)], whereas a spherical shape is observed in the calcined CeO_2 - ZrO_2 powder [Fig 2(d)]. To elucidate whether this change in shape is related to the impregnation process or to the calcination at 700°C, micrographs of calcined ZrO_2 powder and of CeO_2 - ZrO_2 powder before calcination at 700°C are also shown in Fig. 2. It is observed that an ellipsoidal shape is also observed in the powder after CeO_2 impregnation [Fig. 2(c)], whereas both ZrO_2 starting powder and CeO_2 -coated ZrO_2 powder present spherical shape after



Fig. 1. XRD patterns of the hydrothermally synthesized ZrO_2 powder (a), and the calcined 10 mol% CeO₂-coated ZrO_2 powder (b).

	-		
Powder	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (Å)
ZrO ₂ Calcined 10 mol% CeO ₂ -coated ZrO ₂	49.0 18.0	0.25 0.18	192.7 404.0

Table I. Textural Properties of the Powders

Table II. Density and Relative Density of the Ceramics

Density (g/cm ³)	Relative density (%)
5.78	97.9
5.85	99.0
	Density (g/cm ³) 5.78 5.85

calcination at 700°C. Thus, it can be concluded that the change in shape is related to the calcination process. The grain size of both ZrO_2 starting powder and calcined CeO_2 - ZrO_2 powder remains below 100 nm.

The Table II shows density and relative density of the ceramics as a function of holding time. The relative density of the sintered ceramics is higher than 97% in both cases. A gradual color change along the axial direction from brown in the core to orange at the edge was observed on the cross-sectioned ceramic sintered at 1200°C for 5 min, whereas a homogeneous brown color was observed for the ceramic sintered without holding time. No micro- or macrocracks were observed in the ceramics, conversely to the reported result by Huang *et al.* for similar materials.²³

The SEM micrographs of the 10 mol% CeO_2 -doped ZrO_2 ceramics sintered at 1200°C for 5 min, and without holding time are shown in Fig. 3. We analyzed the fracture surface to avoid possible sample oxidation during polishing and etching. In the ceramic sintered for 5 min, a graded microstructure is observed. The average grain size in the edge area is in the range 160–260 nm, whereas in the core area, significantly finer grains with sizes between 60 and 100 nm are observed. On the other hand, a homogeneous microstructure with grain sizes about 40–70 nm in the whole ceramic is observed in the ceramic sintered without holding time.

The Raman spectra of the ceramics sintered at 1200°C without holding time, and for 5 min are shown in Figs. 4 and 5, respectively. In both ceramics, a band at around 2100 cm^{-1} is observed. This band has been attributed to the optical transition band, related to ${}^{2}F_{7/2} \leftrightarrow {}^{2}F_{5/2}$ electronic transition of Ce³⁺ ion.³¹ The Raman bands below 700 cm⁻¹ are attributed to phonon modes. For the ceramic sintered without holding time, peaks at 165, 265, 320, 465, 612, and 643 cm^{-1} appeared. These peaks correspond to the six Raman bands predicted for theoretical tetragonal zirconia, and have been found for previous authors.^{32,33} No significant differences were observed in the spectra measured at the surface and core area of the cross-sectioned ceramic. However, a slight difference in the intensity ratio of peaks at 265 and 320 cm⁻¹ is observed, $I_{265}/I_{320} = 1.72$ and 1.34 for the surface and core area, respectively. This may be related with the symmetry change associated with the observed metastable tetragonal phases (see Rietveld analysis below).

Raman spectra for the ceramic sintered for 5 min show significant differences when measured in the core area or the surface of the ceramic, according to the observed differences in the microstructure. For the core area, where the ceramic presents the smaller grain size, six bands corresponding to tetragonal phase are found. However, the spectrum measured in the surface shows major bands at 185, 338, 480, 625, and 639 cm⁻¹ with minor peaks at 228, 267, 309, 387, 509, 542, and 565 cm⁻¹. The major bands at 185, 338, and 480 cm⁻¹ are assigned to the monoclinic phase.³²⁻³⁴ The bands at 267, 625, and 640 cm^{-1} are assigned to the tetragonal phase. Two main differences have been reported for Raman spectra corresponding to the monoclinic and tetragonal phases³³ the : band at 480 cm⁻¹ is stronger than the band at 640 cm⁻¹ for the monoclinic phase and there are some small bands between 480 and 640 cm⁻¹ for this phase, but these weak bands are absent for the tetragonal one. Regarding the minor bands at 309 and 387 cm^{-1} , they can be related to the pyrochlore phase Ce₂Zr₂O₇. It has been reported^{35,36} that this phase gives a strong band at 295 cm⁻¹ and four weak bands at 391, 448, 497, and 590 cm⁻¹. It can be concluded that the Raman spectrum measured at the ceramic surface is due to mixed monoclinic, tetragonal, and pyrochlore phases. When the spectrum is measured in an intermediate region between the core area and the surface of the ceramic, the six bands corresponding to tetragonal phase are clearly



Fig. 2. SEM micrographs of the hydrothermally synthesized ZrO_2 starting powder (a), calcined ZrO_2 powder (b), 10 mol% CeO₂-coated ZrO_2 powder (c), and calcined 10 mol% CeO₂-coated ZrO_2 powder (d).



Fig. 3. SEM micrographs of the surface (a) and core (b) area of the ceramic sintered at 1200°C for 5 min, and the surface (c) and core (d) area of the ceramic sintered at 1200°C without holding time.



Fig. 4. Raman spectra measured in the ceramic sintered at 1200°C without holding time. Full Raman spectra (a) Range of interest (b). t, tetragonal phase.



Fig. 5. Raman spectra measured in the ceramic sintered at 1200°C for 5 min. Full Raman spectra (a) Range of interest (b). t, tetragonal phase; m, monoclinic phase; and p, pyrochlore phase.

observed, however, small bands between 480 and 640 cm⁻¹ appear, pointing to a trace of monoclinic phase. In addition, the band observed at 387 cm⁻¹ is related to a trace of pyrochlore phase. According to these results, it can be concluded that this ceramic shows a graded phase distribution from core area to surface area.

Rietveld refinements corresponding to the ceramics sintered at 1200°C without holding time, and for 5 min are given in Fig. 6.

The Rietveld analysis corresponding to the ceramic sintered without holding time was initially modeled as completely tetragonal (space group $P4_2/nmc$), assuming Ce/Zr are randomly distributed at the special positions 2a and O²⁻ ions occupy the 4d positions. Under this assumption, a large value of the weighted residual, $R_{\rm wp}$, was obtained in spite of the excellent quality of the diagram (expected residual $R_e = 3.46$). Moreover, the high value of the observed FWHM (0.2565° 2θ) and asymmetry of the more relevant Bragg reflection (at about 30° 20) let us suspect the existence of a second phase highly overlapped with the tetragonal phase. As a first choice, we introduced in the model, the cubic phase (fluorite structure, space group Fm3m). However, this hypothesis was rejected as the R_{wp} residual increased. Finally, we introduced the metastable t' phase, and the decrease in the R_{wp} residual showed that the system is formed by two phases, of which the major crystalline phase is metastable tetragonal, t', 90.94%, and the minor phase is tetragonal 9.06% (Table III). In the last cycle, the number of fitted parameters was 57.

For the ceramic sintered for 5 min, the Rietveld refinement indicates the formation of three phases (Table IV), of which the major crystalline phase is tetragonal (82.5%), and the minor phases are monoclinic (15.1%) and Ce₂Zr₂O₇ (pyrochlore structure, 2.4%). In the structure of the stoichiometric pyrochlore, A₂B₂O₇ (space group *Fd3m*), the Ce and Zr atoms occupy the 16*c* and 16*d* positions, and oxygen atoms occupy the 48*f*, 8*a*, and 8*b* positions. However, refinement of the respective occupation factors revealed that Ce ions are placed preferentially in the 16*c* position, whereas Zr ions occupy the 16*d* Wycoff position. The structure of pyrochlore oxides may be described as an ordered cubic closed-packed array of cations with the oxygen ions occupying 7/8 of the tetrahedral sites. The stoichiometric phase is a semiconductor. However, it has been reported that by



Fig. 6. Rietveld refined powder XRD data for the ceramic sintered at 1200°C without holding time (a), and for 5 min (b).

 Table III.
 Rietveld Refinement of the 10 mol% CeO₂-ZrO₂

 Ceramic Sintered at 1200°C without Holding Time

Phase	Tetragonal	ť
Fraction (%)	9.06	90.94
a = b (Å)	3.65	3.62
c (Å)	5.20	5.21
R _p	12.	7
R _{wp}	20.	9
Rexp	4.2	6
γ^{2}	4.9	1
$O_1 z$	0.061	0.022

 Table IV.
 Rietveld Refinement of the 10 mol% CeO₂-ZrO₂

 Ceramic Sintered at 1200°C for 5 min

Phase	Tetragonal	Monoclinic	Pyrochlore I
Fraction (%)	82.50	15.10	2.40
a (Å)	3.62	5.18	10.63
b (Å)	3.62	5.20	10.63
$c(\mathbf{A})$	5.21	5.32	10.63
R _p		7.13	
R _{wp}		9.01	
Rexp		4.53	
χ^2		3.95	
Õ ₁ z	0.048	0.36	0.12

modifying the stoichiometry, the electrical properties can be changed from insulating to metallic behavior.^{37,38} A detailed study of the electric properties will be given elsewhere.

IV. Discussion

The differences in microstructure and phases distribution observed in the ceramics prepared with the two different sintering conditions reveal the remarkable effect of the sintering time. This is related to the reduction of Ce^{4+} to Ce^{3+} , which is promoted by the strongly reducing environment and the very low oxygen partial pressure created by the die and punches during sintering. Different studies have shown that the content of Ce_2O_3 depends on the atmosphere (N₂, Ar, vacuum), the partial oxygen pressure, and the temperature, and amounts of Ce^{3+} as high as 90% have been reported for Ce-TZP ceramics sintered in graphite furnace.^{25,39}

The very fast SPS cycle used when sintering the ceramic at 1200°C without holding time inhibits the complete reduction of Ce^{4+} . Although some degree of reduction is pointed out by the Raman band observed at 2100 cm⁻¹ (Fig. 4), and also by the brown/orange color in the samples,^{17,23} the tetragonal phase stabilization is achieved in the CeO₂-ZrO₂ solid solution. The t and t' phases have been found to be the only phases in the different areas of the ceramic, which is in agreement with the phase diagram reported by Yashima et al.40 for CeO2-ZrO2 ceramics. For 10% CeO2-ZrO2 composition, at the sintering temperature (1200°C) and room temperature, the phases in the diagram are t and t', respectively. In our work, the fast cooling ramp achieved in SPS allows the retention, 10% of the t-phase, at room temperature. On the other hand, this very fast sintering cycle inhibits the grain growth giving place to a nanostructured ceramic with grain size similar to the initial nanometric particle size.

When sintering at 1200°C for 5 min, the reduction of Ce⁴⁺ to Ce³⁺ propagates from the edge area to the inside of the ceramic, giving place to the observed microstructural differences in the ceramic. In the edge area, where all Ce4+ ions are reduced to Ce^{3+} , the relevant phase diagram is the ZrO_2 -Ce₂O₃ system, reported by Leonov et al.⁴¹ According to this phase diagram, a cubic Ce₂Zr₂O₇ compound with a pyrochlore structure is in equilibrium with m-ZrO2-Ce2O3 solid solution below 1000°C. The Raman spectra measured in the surface area confirm the presence of monoclinic and pyrochlore phases. In an intermediate area, the Raman spectra confirm the presence of monoclinic and pyrochlore phases, together with traces of tetragonal phase, pointing to a partial reduction of Ce^{4+} to Ce^{3+} . The stabilization of the *t*-phase in the CeO₂-ZrO₂ solid solution in the core area of this ceramic indicates a low degree of reduction, similar to the one described in the ceramic sintered without holding time.

The coarser grain size observed in the surface area of this ceramic is also a consequence of the complete reduction of Ce^{4+} to Ce^{3+} in this area. The high amount of vacancies generated in the structure by the trivalent cation Ce^{3+} promotes a higher species diffusion, which results in enhanced sintering and grain coarsening. Thus, the graded CeO_2 reduction that takes place when the sintering temperature is allowed to stabilize for a short time results in a graded material with a gradient in microstructure, grain size, and phases distribution.

V. Conclusions

The combination of a two-step powder synthesis technique and spark plasma sintering allows the processing of nearly fully densified 10 mol% CeO₂-doped ZrO₂. The very fast SPS cycle used when sintering the ceramic at 1200°C without holding time allows the stabilization of the tetragonal phase, despite the highly reducing atmosphere generated during sintering, and the retention of the nanostructure, with grain sizes of 40–70 nm and high relative density, 97.9%. When stabilizing the sintering temperature for 5 min, a graded material with presence of monoclinic and pyrochlore phases in the surface area and tetragonal phase in the core area is obtained. This graded phase distribution, together with the observed gradient in grain size, with 60-100 nm in the core area and 160-260 nm in the surface area, is consequence of the gradual reduction of Ce⁴⁺ to Ce³⁺ in the graphite environment during SPS.

Acknowledgments

Dr. Cruz thanks Junta de Andalucía (TEP-1048) for her fellowship. The financial support for this work has been obtained from the Spanish Ministerio de Ciencia e Innovación (ENE2009-14522-C05-01) and (ENE2009-14522-C05-03) co-financed by FEDER funds from the European Union and from Junta de Andalucía (P09-TEP-5454).

References

¹W. C. Maskell, "Progress in the Development of Zirconia Gas Sensors," *Solid State Ionics*, **134**, 43–50 (2000).

²S. C. Singhal, "Solid Oxide Fuel Cells for Stationary, Mobile, and Military Applications," *Solid State Ionics*, **152–153**, 405–10 (2002).
³F. Gutiérrez-Mora, D. Gomez-García, M. Jiménez-Melendo, and A. Dom-

³F. Gutiérrez-Mora, D. Gomez-García, M. Jiménez-Melendo, and A. Domínguez-Rodríguez, "Experimental Assessment of Plasticity of Nanocrystalline 1.7 mol% Yttria Tetragonal Zirconia Polycrystals," *J. Am. Ceram. Soc.*, **88**, 1529–35 (2005).

4S. Boulfrad, E. Djurado, and J. Fouletier, "Electrochemical Characterization of Nanostructured Zirconias," *Solid State Ionics*, 180, 978–83 (2009).

⁵E. Zapata-Solvas, D. Gómez-García, C. García-Gañán, and A. Domínguez-Rodríguez, "High Temperature Creep Behaviour of 4 mol% Yttria Tetragonal Zirconia Polycrystals (4-YTZP) with Grain Sizes Between 0.38 and 1.15 μm," *J. Eur. Ceram. Soc.*, **27**, 3325–9 (2007).

⁶Y. J. He, L. Winnubst, A. J. Burggraaf, H. Verweij, P. G. T. vanderVast, and B. deWith, "Grain-Size Dependence of Sliding Wear in Tetragonal Zirconia Polycrystals," *J. Am. Ceram. Soc.*, **79**, 3090–6 (1996).

⁷M. Trunec and Z. Chlup, "Higher Fracture Toughness of Tetragonal Zirconia Ceramics Through Nanocrystalline Structure," *Scr. Mater.*, **61**, 56–9 (2009).

⁸J. A. Montoya, E. Romero-Pascual, C. Gimon, P. Del Angel, and A. Monzón, "Methane Reforming with CO₂ Over Ni/ZrO₂-CeO₂ Catalysts Prepared by Sol-Gel," *Catal. Today*, **63**, 71–85 (2000).

by Sol-Gel," *Catal. Today*, **63**, 71–85 (2000). ⁹A. Muto, T. Bhaskar, Y. Kaneshiro, Y. Sakata, Y. Kusano, and K. Murakami, "Preparation and Characterization of Nanocrystalline CeO₂–ZrO₂ Catalysts by Dry Method: Effect of Oxidizing Conditions," *Appl. Catal. A General*, **275**, 173–81 (2004).

275, 173–81 (2004). ¹⁰R. H. J. Hannink, P. M. Kelly, and B. C. Muddle, "Transformation Toughening in Zirconia-Containing Ceramics," *J. Am. Ceram. Soc.*, **83**, 461– 87 (2000).

 87 (2000).
 ¹¹J. Wang, X. H. Zheng, and S. Stevens, "Fabrication and Microstructure– Mechanical Property Relationships in Ce-TZPs," *J. Mater. Sci.*, 27, 5348–56 (1992).

(1992).
 ¹²S. de Bernardi-Martín, E. Zapata-Solvas, D. Gómez-García, A. Domín-guez-Rodríguez, F. J. Guzmán-Vázquez, and J. Gómez-Herrero, "On the High-Temperature Plasticity of Ceria-Doped Zirconia Nanostructured Polycrystals," *Key Eng. Mater.*, **423**, 61–6 (2010).
 ¹³M. Boaro, A. Trovarelli, J.-H. Hwang, and T. O. Mason, "Electrical and

¹³M. Boaro, A. Trovarelli, J.-H. Hwang, and T. O. Mason, "Electrical and Oxygen Storage/Release Properties of Nanocrystalline Ceria–Zirconia Solid Solutions," *Solid State Ionics*, **147**, 85–95 (2002).

¹⁴Y.-P. Fu, S.-H. Hu, and B.-L. Liu, "Structure Characterization and Mechanical Properties of CeO₂-ZrO₂ Solid Solution System," *Ceram. Int.*, **35**, 3005–11 (2009).

 ^{15}Z . X. Yuan, J. Vleugels, and O. Van Der Biest, "Preparation of Y₂O₃-Coated ZrO₂ Powder by Suspension Drying," *J. Mater. Sci. Lett.*, **19**, 359–61 (2000).

¹⁶S. G. Huang, K. Vanmeensel, O. Van Der Biest, and J. Vleugels, "Influence of CeO₂ Reduction on the Microstructure and Mechanical Properties of Pulsed Electric Current Sintered Y₂O₃-CeO₂ Co-Stabilized ZrO₂ Ceramics," *J. Am. Ceram. Soc.*, **90**, 1420–6 (2007).

Am. Ceram. Soc., 90, 1420–6 (2007).
 ¹⁷Y. M. Chiang, E. B. Lavik, I. Kosacki, H. L. Tuller, and J. Y. Ying,
 "Nonstoichiometry and Electrical Conductivity of Nanocrystalline CeO_{3-x},"
 J. Electroceram., 1, 7–14 (1997).

J. Electroceram., 1, 7–14 (1997). ¹⁸S. C. Liao, Y. J. Chen, B. H. Kear, and W. E. Mayo, "High Pressure/ Low Temperature Sintering of Nanocrystalline Alumina," *Nanostructured Mater.*, **10**, 1063–79 (1998).

¹⁹M. Omori, "Sintering, Consolidation, Reaction and Crystal Growth by the Spark Plasma System (SPS)," *Mater. Sci. Eng. A*, **287**, 183–8 (2000).

²⁰Z. A. Munir, U. Anselmi-Tamburini, and M. Ohyanagi, "The Effect of Electric Field and Pressure on the Synthesis and Consolidation of Materials: A Review of the Spark Plasma Sintering Method," *J. Mater. Sci.*, **41**, 763–77 (2006).

(2006).
 ²¹U. Anselmi-Tamburini, J. E. Garay, and Z. A. Munir, "Fast Low-Temperature Consolidation of Bulk Nanometric Ceramic Materials," *Scr. Mater.*, 54, 823–8 (2006).
 ²²T. Xu, P. Wang, P. Fang, Y. Kan, L. Chen, J. Vleugels, O. Van der Biest,

²²T. Xu, P. Wang, P. Fang, Y. Kan, L. Chen, J. Vleugels, O. Van der Biest, and J. Van Landuyt, "Phase Assembly and Microstructure of CeO₂-Doped ZrO₂ Ceramics Prepared by Spark Plasma Sintering," *J. Eur. Ceram. Soc.*, **25**, 3437–42 (2005).
²³S. G. Huang, O. Van Der Biest, J. Vleugels, K. Vanmeensel, and L. Li,

²³S. G. Huang, O. Van Der Biest, J. Vleugels, K. Vanmeensel, and L. Li, "Characterization of Y₂O₃, CeO₂ and Y₂O₃+CeO₂ Doped FGM Tetragonal ZrO₂ Ceramics by Spark Plasma Sintering," *Key Eng. Mater.*, **333**, 231–4 (2007).

(2007).
 ²⁴K.-H. Heussner and N. Claussen, "Yttria and Ceria-Stabilized Tetragonal Zirconia Polycrystals (Y-TZP, Ce-TZP) Reinforced with Al₂O₃," *J. Eur. Ceram. Soc.*, 5, 193–200 (1989).

²⁵S. Huang, L. Li, J. Vleugels, P. Wang, and O. Van der Biest, "Thermodynamic Prediction of the Nonstoichiometric Phase Zr_{1-z}Ce_zO_{2-x} in the ZrO₂-CeO_{1.5}-CeO₂ System," *J. Eur. Ceram. Soc.*, 23, 99–106 (2003).
 ²⁶J. Rodriguez-Carvajal, "FULLPROF: A Program for Rietveld Refinement

²⁶J. Rodriguez-Carvajal, "FULLPROF: A Program for Rietveld Refinement and Pattern Matching Analysis" in Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, 127–130 (1990).
²⁷W. A. Dollase, "Correction of Intensities for Preferred Orientation in

²⁷W. A. Dollase, "Correction of Intensities for Preferred Orientation in Powder Diffractometry: Application of the March Model," *J. Appl. Crystallogr.*, **19**, 267–72 (1986).
²⁸J. Kaspar and P. Formagiero, "Structural Properties and Thermal Stabi-

²⁸J. Kaspar and P. Formagiero, "Structural Properties and Thermal Stability of Ceria-zirconia and Related Materials"; p. 217 in *Catalysis by Ceria and Related Materials*, Edited by A. Trovarelli. Imperial College press, London, 2002.

²⁹G. Balducci, J. Kaspar, P. Fornasiero, M. Graziani, M. S. Islam, and J. D. Gale, "Computer Simulation Studies of Bulk Reduction and Oxygen Migration in CeO₂-ZrO₂ Solid Solutions," *J. Phys. Chem. B*, **101**, 1750–3 (1997).

³⁰G. Balducci, M. S. Islam, J. Kaspar, P. Fornasiero, and M. Graziani, "Bulk Reduction and Oxygen Migration in the Ceria-Based Oxides," *Chem. Mater.*, **12**, 677–81 (2000).

³¹T. Otake, H. Yugami, H. Naito, K. Kawamura, T. Kawada, and J. Mizusaki, "Ce³⁺ Concentration in ZrO₂-CeO₂-Y₂O₃ System Studied by Electronic Raman Scattering," *Solid State Ionics*, **135**, 663–7 (2000).

³²M. Rumruangwong and S. Wongkasemjit, "Synthesis of Ceria-Zirconia Mixed Oxide from Cerium and Zirconium Glycolates Via Sol-Gel Process and its Reduction Property," *Appl. Organomet. Chem.*, **20**, 615–25 (2006).

³³W. Miśta, T. Rayment, J. Hanuza, and L. Macalik, "Synthesis and Characterization of Metastable CeO₂-ZrO₂ Solid Solution Obtained by Polymerized Complex Method," *Mater. Sci. Poland*, **22**, 153–70 (2004).

³⁴M. Li, Z. Feng, G. Xiang, P. Ying, Q. Xin, and C. Li, "Phase Transformation in the Surface Region of Zirconia Detected by UV Raman Spectroscopy," *J. Phys. Chem. B*, **105**, 8107–11 (2001).

copy," *J. Phys. Chem. B*, **105**, 8107–11 (2001). ³⁵Z. Hui, G. Nicolas, V. Françoise, and P. Michèle, "Preparation and Electrical Properties of a Pyrochlore-Related Ce₂Zr₂O_{8-x}," *Solid State Ionics*, **160**, 317–26 (2003). ³⁶T. Omata, H. Kishimoto, S. Otsuka-Yao-Matsuo, N. Ohtori, and N.

³⁶T. Omata, H. Kishimoto, S. Otsuka-Yao-Matsuo, N. Ohtori, and N. Umesaki, "Vibrational Spectroscopy and X-ray Diffraction Studies of Cerium Zirconium Oxides with Ce/Zr Composition Ratio=1 Prepared by Reduction and Successive Oxidation of t'-(Ce_{0.5}Zr_{0.5})O₂ Phase," J. Solid State Chem., 147, 573–83 (1999).

147, 573–83 (1999). ³⁷J. B. Thomson, A. R. Armstrong, and P. G. Bruce, "An Oxygen-Rich Pyrochlore with Fluorite Composition," *J. Solid State Chem.*, **148**, 56–62 (1999).

(1999). ³⁸T. Baidya, M. S. Hegde, and J. Gopalakrishnan, "Oxygen-Release/Storage Properties of Ce_{0.5}M_{0.5}O₂ (M=Zr, Hf) Oxides: Interplay of Crystal Chemistry and Electronic Structure," *J. Phys. Chem. B*, **111**, 5149–54 (2007).

³⁹S. Huang, L. Li, O. Van Der Biest, and J. Vleugels, "Influence of the Oxygen Partial Pressure on the Reduction of CeO₂ and CeO₂-ZrO₂ Ceramics," *Solid State Sci.*, **7**, 539–44 (2005).

 40 M. Yashima, H. Arashi, M. Kakihana, and M. Yoshimura, "Raman-Scattering Study of Cubic-Tetragonal Phase-Transition in $Zr_{1-x}Ce_xO_2$ Solid-Solution," *J. Am. Ceram. Soc.*, **77**, 1067–71 (1994).

tion, \overline{J} , Am. Ceram. Soc., 77, 106/-/1 (1994). ⁴¹A. I. Leonov, A. B. Andreeva, and E. K. Keler, "Influence of the Gas Atmosphere on the Reaction of Zirconium Dioxide with Oxides of Cerium," Izq. Akad. Nauk SSSR Neorganicheskie Mater., **2**, 137-44 (1966).