

3 Phase assembly and electrical conductivity of spark plasma 4 sintered CeO₂-ZrO₂ ceramics

5 Rosalía Poyato · Sylvia A. Cruz ·
6 Francisco L. Cumbreira · Berta Moreno ·
7 Eva Chinarro · José A. Odriozola

8 Received: 30 January 2014 / Accepted: 27 May 2014
9 © Springer Science+Business Media New York 2014

10 **Abstract** Ce_xZr_{1-x}O₂ ($x = 0.10, 0.16$ and 0.33) nano-
11 crystalline powders were obtained by a two-step synthesis
12 technique and sintered by spark plasma sintering (SPS). As
13 consequence of the reduction of Ce⁴⁺ to Ce³⁺ species by
14 carbon in the graphite environment in SPS, phase assem-
15 blies including tetragonal, monoclinic and pyrochlore
16 phases were generated in the ceramics during the sintering
17 process. The electrical conductivity was highly dependent
18 on phase assembly and atmosphere (N₂, H₂ and O₂). A
19 significant decrease in the activation energy was noticed in
20 the ceramics with high pyrochlore content when measuring
21 the conductivity in H₂ atmosphere, consequence of the
22 strong reduction promoted in these ceramics during the
23 measurement. Equal conduction behavior with similar
24 activation energy was observed in all the ceramics when
25 measuring in O₂ atmosphere.

27 **Keywords** CeO₂-ZrO₂ · Spark plasma sintering ·
28 Pyrochlore · Electrical conductivity

A1 R. Poyato (✉) · S. A. Cruz · J. A. Odriozola
A2 Instituto de Ciencia de Materiales de Sevilla, Univ. de Sevilla-
A3 CSIC, Avda. Américo Vespucio, 49, 41092 Seville, Spain
A4 e-mail: rosalia.poyato@icmse.csic.es

A5 F. L. Cumbreira
A6 Dep. Física de la Materia Condensada, Univ de Sevilla,
A7 41080 Seville, Spain

A8 B. Moreno · E. Chinarro
A9 Instituto de Cerámica y Vidrio, CSIC, c/Kelsen 5,
A10 28049 Cantoblanco, Madrid, Spain

Introduction

CeO₂-ZrO₂-based materials have been widely investigated
due to their great potential for different applications, such
as gas sensors, solid oxide fuel cells (SOFC) or catalytic
materials [1–4].

This system has been shown to be a mixed conductor
unlike most stabilized zirconias. Whereas the latter are
usually pure ionic conductors, the former can exhibit large
electronic contributions at moderate temperatures and
oxygen activities [5–8]. The defect structure of CeO₂-ZrO₂
has been described by different authors [5, 7–9] and can be
summarized as follows. Due to charge neutrality consid-
erations, a Ce⁴⁺ ion substituting a Zr⁴⁺ cannot affect any
additional creation of oxygen vacancies beyond the inher-
ent defect concentration level. However, the presence of
Ce⁴⁺ ions on Zr⁴⁺ sites affects the point defect equilibria
involving oxygen vacancies, as the formation of oxygen
vacancies might be favored by the large size difference of
the two cations ($r_i(\text{Zr}^{4+}) = 0.72 \text{ \AA}$; $r_i(\text{Ce}^{4+}) = 0.87 \text{ \AA}$, for
sixfold coordination) [5, 6, 9, 10]. The second aspect is that
Ce⁴⁺ ion is easily reduced to Ce³⁺ under suitably low
oxygen partial pressures (10^{-11} to 10^{-19} atm) [11, 12];
therefore, charged oxygen vacancies are produced. These
vacancies are coupled to free electrons localized on Ce³⁺
substitutional defects, giving rise to electronic conductivity
through electron hopping between cerium ions [5, 7],
which is strongly dependent on the ceria content [5].

The mixed conduction makes this system an interesting
material for application as SOFC anode [1], and correlation
between electrical and structural properties of the ceria-
zirconia system has been approached in recent studies [7,
13–16]. Boaro et al. [16] have carried out a complete study
of the effects of redox history on structural, chemical and
electrical properties of Ce_xZr_{1-x}O₂ ($x = 0.20, 0.50$ and

63 0.80) solid solution in order to explore the suitable oper- 111
64 ational conditions for an optimization of their use as 112
65 electroactive components for SOFC anodes.

66 Recently, we reported on the processing and micro- 113
67 structural study of nanostructured 10 mol% CeO₂-ZrO₂ 114
68 ceramics prepared by spark plasma sintering (SPS) [17]. 115
69 This technique has emerged as a powerful tool in ceramics 116
70 processing, as it allows fast densification of ceramics at 117
71 relatively low temperatures and pressures by the simulta- 118
72 neous application of pressure and a low DC voltage to the 119
73 graphite mold during heating [18–20]. We have shown that 120
74 the highly reducing atmosphere created by the graphite 121
75 environment during SPS promoted the gradual reduction of 122
76 Ce⁴⁺ to Ce³⁺, giving place to presence of pyrochlore phase 123
77 when sintering at 1200 °C for 5 min. Several authors have 124
78 shown that the reduction of metastable tetragonal phase, 125
79 denoted as *t'* phase, at temperatures ≥1050 °C leads to 126
80 pyrochlore phases (Ce₂Zr₂O_{7+δ}) [12, 14, 21–23]; however, 127
81 to the best of our knowledge, no studies have been pub- 128
82 lished on the appearance of these phases in spark plasma 129
83 sintered CeO₂-ZrO₂ ceramics with different CeO₂ doping 130
84 concentrations and the effect of phase formation on the 131
85 conductivity in this system. 132

86 In this study, 10, 16 and 33 mol% CeO₂-doped ZrO₂ 133
87 powders were obtained by means of a two-step synthesis 134
88 route and subsequently sintered by SPS. Phase assembly of 135
89 the ceramics was analyzed by X-ray diffraction and Riet- 136
90 veld refinement. The effect of the CeO₂ content on the 137
91 phase assembly of the ceramics was investigated. The 138
92 electrical conductivity as a function of temperature 139
93 (200–900 °C) was analyzed in three different atmospheres. 140
94 The structural characterization was of prime relevance for 141
95 understanding the electrical conductivity results as the 142
96 different conduction mechanisms found were related to the 143
97 phase assembly of the ceramics.

98 Experimental procedure

99 Powder synthesis and characterization

100 According to the phase diagram for the system Ce₂O₃- 145
101 ZrO₂ [24], the compound Ce₂Zr₂O₇ with pyrochlore 146
102 structure is in equilibrium with monoclinic/tetragonal 147
103 phases above and below 1000 °C, respectively, for com- 148
104 positions with Zr/Ce atomic ratios between 1.3 (44 mol% 149
105 Ce₂O₃) and 32.3 (3 mol% Ce₂O₃). Thus, the formation of 150
106 the pyrochlore cubic structure stabilizes the ZrO₂ tetrago- 151
107 nal phase, promoting an increase of ionic conductivity by 152
108 increase of the oxygen vacancies, as a consequence of the 153
109 substitution of Ce³⁺ for Zr⁴⁺. Using this phase diagram, 154
110 the CeO₂ compositions (10, 16 and 33 mol% CeO₂) were 155

selected among those that stabilize the tetragonal phase by 111
the formation of pyrochlore phase. 112

Ce_{0.10}Zr_{0.90}O₂ (CeZr10), Ce_{0.16}Zr_{0.84}O₂ (CeZr16) and 113
Ce_{0.33}Zr_{0.67}O₂ (CeZr33) mixed oxides were synthesized by 114
a two-step synthesis procedure. In a first step, a hydro- 115
thermal route was followed to synthesize nanocrystalline 116
ZrO₂ powder. Zirconyl nitrate hydrate (ZrO(NO₃)_x·xH₂O, 117
0.5 M, <90 % purity) and sodium hydroxide (NaOH, 5 M) 118
were mixed together and sonicated for 30 min. Later, 119
10 mL of the solution was disposed in the hydrothermal 120
vessel with 2 mL of ethanol, closed and heated in a furnace 121
for 5 h at 200 °C. When the vessel achieved room tem- 122
perature, the solid was washed with distilled water and 123
dried at 100 °C for 1 h. In a second step, cerium oxide was 124
deposited onto the ZrO₂ particles by the impregnation 125
method. The adequate amount of 1 M Ce(NO₃)₃·6H₂O 126
solution (99.5 % purity) was added to the solid in order to 127
obtain 10, 16 or 33 mol% CeO₂-ZrO₂ powders. The 128
resulting slurries were then dried for 12 h at 100 °C. 129
Finally, the ceramic powders were calcined at 700 °C for 130
4 h. The powders were suspended in aqueous solution and 131
subjected to ultrasonic agitation in order to reduce 132
agglomeration before their analysis. 133

X-ray diffraction (PANalytical X'Pert Pro diffractome- 134
ter) was used for phase identification of the powders. 135
Diffraction patterns were recorded using Cu Kα radiation 136
over a 2θ range of 10°–90° and a position-sensitive 137
detector using a step size of 0.05°2θ and a counting time of 138
1 s per step. 139

The cerium and zirconium contents of the samples were 140
determined by X-ray fluorescence spectrometry (XRF- 141
Panalytical AXIOS PW4400) sequential spectrophotometer 142
with a rhodium tube as the source of radiation. 143

Ceramics processing and characterization 144

SPS (Model 515S, SPS Dr Sinter Inc., Kanagawa, Japan) of 145
the ceramic powders was performed in a vacuum in a 146
15-mm-diameter cylindrical graphite die/punch setup, 147
under a uniaxial pressure of 50 MPa at 1200 °C for 5 min 148
or without holding time. The heating rate was 100 °C/min. 149
The applied pressure was maintained throughout the entire 150
thermal cycle. Hereinafter, we will refer to the sintered 151
samples as CeZr10-0 min, CeZr10-5 min, CeZr16-0 min 152
and CeZr33-0 min. Temperature was measured by using a 153
thermocouple, which was placed in a bore hole in the 154
middle part of the graphite die. The sintered ceramics of 155
approximately 15 mm × 2 mm were polished in order to 156
eliminate the surface carbon. Density of the ceramics was 157
determined using the Archimedes method, using water as 158
the immersion liquid. Theoretical density for each com- 159
position was calculated according to: 160

$$\text{Theoretical density} = (\text{density}(\text{CeO}_2)) * \text{wt}\%(\text{CeO}_2) + (\text{density}(\text{ZrO}_2)) * \text{wt}\%(\text{ZrO}_2).$$

162 In order to approach phase identification and structural
163 characterization, powder diffraction patterns were collected
164 on the polished, cross-section surfaces of the ceramics. The
165 step scan technique was used with a step size of $0.02^\circ 2\theta$
166 and a counting time of 10 s at each point.

167 Rietveld refinements were performed using the FULL-
168 PROF software [25]. In this method, a least-squares
169 refinement of a crystallographic model is performed until a
170 satisfactory fit is achieved between the theoretical dif-
171 fractogram and the experimental data. A pseudo-Voigt
172 function was chosen to describe the peak shape, and the
173 refinement included the following parameters: (1) the
174 background, generated by linear interpolation of a set of
175 background points with refinable heights; (2) the scale
176 factors; (3) the global instrumental parameters (zero-point
177 2θ shift and systematic shifts, depending on transparency
178 and off-centering of the sample); (4) the lattice parameters
179 for all phases; (5) the profile parameters (Caglioti half-
180 width parameters and the mixing parameter, η , of the
181 pseudo-Voigt function) [26]; (6) refinable atom coordi-
182 nates; and (7) occupancy factors for all atomic species.

183 Quantitative phase analysis with the Rietveld method
184 relies on the simple relationship:

$$W_i = S_i(ZMV) / \sum_{i=1}^n S_j(ZMV)_j$$

186 where W_i is the relative weight fraction of the phase i in a
187 mixture of n phases, and S , Z , M and V are, respectively,
188 the Rietveld scale factor, the number of formula units per
189 cell, the mass of the formula unit and the unit cell volume.
190 Among the profile parameters, it can be outlined the full
191 width at half maximum (FWHM), which is usually
192 expressed as a quadratic form in $\tan\theta$, as introduced by
193 Caglioti et al. [27]:

$$(\text{FWHM})^2 = U \tan^2\theta + V \tan\theta + W$$

195 depending on the U , V and W refinable parameters.

196 Taking into account that many materials have non-
197 stoichiometry deviations and different kinds of disorder,
198 the refinement of site occupancy is required. The site
199 occupancy factors (f) can be defined as the fraction of
200 atoms in a particular Wyckoff position in such a way that
201 $f = 1$ indicates full occupancy.

202 The quality of the Rietveld refinement is quantified by
203 several figures of merit [28]: profile residual, R_p , weighted
204 profile residual, R_{wp} , expected residual, R_{exp} , and Bragg
205 residual R_B . In any case, none of these residuals is a sub-
206 stitute for the plots of the observed and calculated patterns,
207 supplemented by the differences plotted on the same scale.

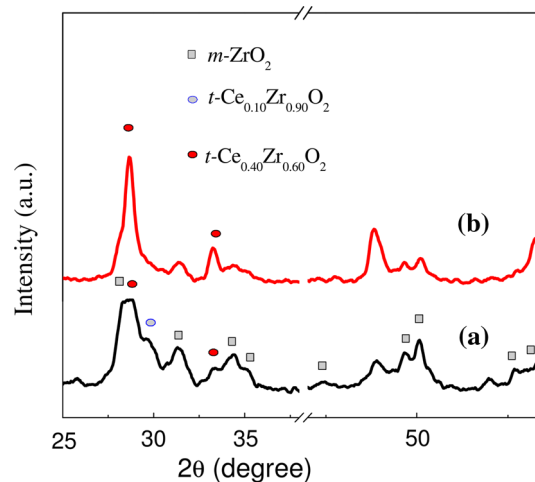


Fig. 1 XRD patterns of the calcined CeO_2 - ZrO_2 powders with 16 mol% CeO_2 (a) and 33 mol% CeO_2 (b)

208 Microstructural investigation was performed by scan-
209 ning electron microscopy (Hitachi S4800 SEM-FEG).

210 Electrical properties were measured by impedance
211 spectroscopy with an Agilent 4294A equipment; two-point
212 measurements were performed on the samples sandwiched
213 between Pt foils that acted as electrodes and that contacted
214 the sample through simple mechanical pressure. Pt paste
215 electrodes were not applied to the samples before testing,
216 since microstructural changes could be induced during
217 electrode firing. The samples were placed in a tubular
218 furnace where atmosphere and temperature were con-
219 trolled. Measurements were acquired in N_2 , H_2 and O_2
220 atmosphere, and oxygen partial pressure was not recorded
221 while measuring, in the frequency range from 40 to 10^7 Hz
222 and varying the temperature from 200 to 900 °C. The
223 conductivity values were determined after fitting the
224 spectra with the Zview software.

225 Results and discussion

226 The XRD patterns for the calcined CeZr16 and CeZr33
227 powders are presented in Fig. 1. It has been published [17]
228 that the presence of monoclinic ZrO_2 phase (JCPDS
229 01-078-0047) in the starting powder is clear. However,
230 when increasing the CeO_2 content to 10 mol%, other
231 phases are found [17]. In the powders with 16 mol% CeO_2 ,
232 the tetragonal solid solution (JCPDS 01-080-0) is present,
233 and the $\text{Ce}_{0.40}\text{Zr}_{0.40}\text{O}_2$ solid solution is found in the pow-
234 ders with 16 and 33 mol% CeO_2 . Also, a decrease in the
235 peaks corresponding to the monoclinic ZrO_2 phase is
236 observed in the two powders with higher CeO_2 content.
237 The observed phases are in agreement with the phase

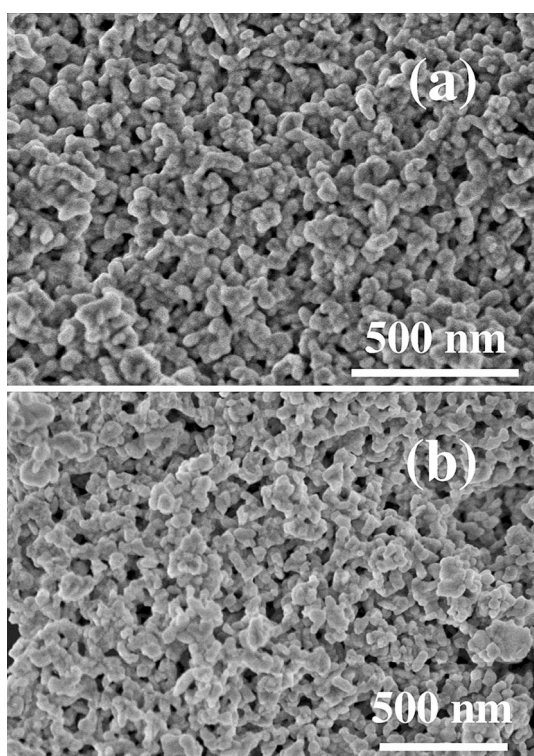


Fig. 2 SEM micrographs of **a** the calcined 16 mol% CeO₂-ZrO₂ powder and **b** the calcined 33 mol% CeO₂-ZrO₂ powder

Table 1 Density, relative density and grain size of the ceramics

Ceramic	Theoretical density (g/cm ³)	Measured density (g/cm ³)	Relative density (%)	Grain size (nm)	
				Core region	Edge region
CeZr16-0 min	5.97	5.85	98.0	50–70	50–70
CeZr33-0 min	6.13	5.60	91.4	40–70	100–150

238 diagram reported by Kaspar et al. [29] for CeO₂-ZrO₂ solid
239 solution. The same crystallite size (20 nm) was obtained
240 for all compositions.

241 The cerium and zirconium contents of the powders,
242 determined by XRF, are identical as the nominal ones.
243 SEM micrographs of the calcined CeZr16 and CeZr33
244 powders show a spherical shape and a grain size lower than
245 100 nm in both of them (Fig. 2). Similar characteristics
246 have been published for the calcined CeZr10 powder [17].

247 Table 1 shows density and relative density of the sintered
248 ceramics. Nearly full densification (>98 % TD) was
249 obtained in the CeZr16-0 min ceramic, similar to the
250 reported result for the CeZr10-0 min and CeZr10-5 min
251 ceramics [17], whereas a lower relative density, 91.4 %,
252 was measured in the ceramic with higher CeO₂ content. No
253 micro- or macrocracks were observed in the ceramics,

254 conversely to the results published by Huang et al. [30]
255 for similar materials. These authors reported the existence
256 of macrocracks in 12 mol% CeO₂-doped ZrO₂ ceramics
257 prepared by SPS and related this fact to the presence of a large
258 amount of monoclinic ZrO₂ phase.

259 Using the experimental X-ray diffraction patterns, Rietveld
260 refinements were carried out in CeZr16-0 min and
261 CeZr33-0 min ceramics. In a first analysis of the CeZr16-
262 0 min ceramic, four phases were discerned, tetragonal,
263 monoclinic, cubic pyrochlore and some residual graphite,
264 this latter most likely being a rest of the graphite foil used
265 during SPS that was not suitably removed. In an earlier
266 study [17], we have shown that the highly reducing
267 atmosphere created by the graphite environment during
268 SPS promotes the reduction of Ce⁴⁺ to Ce³⁺ in CeO₂-ZrO₂
269 ceramics, and the obtained phases are in agreement with
270 the ZrO₂-Ce₂O₃ phase diagram [24].

271 However, during the analysis of the Rietveld refinement
272 of the CeZr16-0 min ceramic, we noted that the pyrochlore
273 amount [54.1(7) wt%] was quite high given the Ce avail-
274 able in the system (16 mol%). Moreover, when refining the
275 occupancy factors, it was found that almost all the Ce is
276 present in the pyrochlore phase, and a composition of
277 Zr_{3.26}Ce_{0.74}O_{7.63} was obtained, which implies that in this
278 phase Ce and Zr are not in 1:1 stoichiometry. Besides that,
279 the reliability factors (i.e., $\chi^2 = 5.60$) are not fully satis-
280 factory, a fact that is particularly true for the R_B and R_F
281 residuals associated with the cubic pyrochlore phase. This
282 disagreement, together with the anomalous stoichiometry
283 of this phase, far from the usual formula A₂B₂O₇ of the
284 pyrochlore oxides, led us to evaluate an alternative model
285 for the pyrochlore structure.

286 In fact, other authors have reported for some particular
287 pyrochlore systems alternative groups of symmetry to the
288 usual cubic $Fd\bar{3}m$. Taking into account the maximal sub-
289 groups of the $Fd\bar{3}m$, Thomson et al. [31] proposed the
290 rhombohedral $R\bar{3}m$ group of symmetry for Ce₂Zr₂O_{7.97},
291 whereas Sasaki et al. [32] found the cubic phase $F\bar{4}3m$ for
292 the composition Ce₂Zr₂O_{7.5}. Kishimoto et al. [33] found
293 the P2₁3 group of symmetry for the Ce₂Zr₂O₈ composition
294 (also called κ -CeZrO₄ phase), although this last group is
295 not a subgroup of the original $Fd\bar{3}m$. In a first stage, we
296 tested these structures for our pyrochlore phase, but the
297 Rietveld refinement worsened in relation to our first con-
298 ventional refinement. In the same way, we have investi-
299 gated, with negative results, the possibility of the δ -phase,
300 reported by Thornber et al. [34]: a fluorite-related structure
301 with different stoichiometries for both kinds of cations.

302 By considering that according to Wuensch et al. [35],
303 pyrochlore is the only oxide in which simultaneous order-
304 disorder transformations take place for both the anion and
305 cation arrays in structure, we proposed a new model with

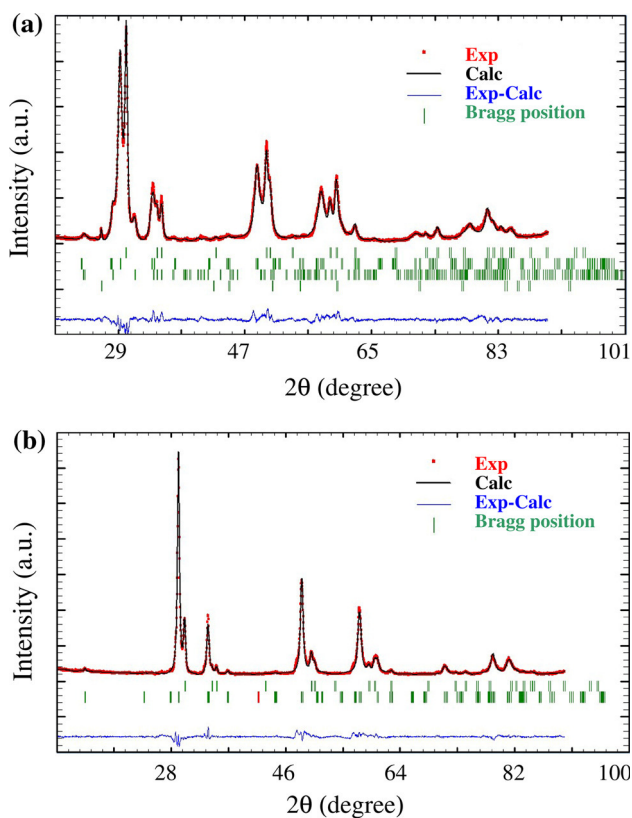


Fig. 3 Rietveld refined powder XRD data for **a** the CeZr16-0 min ceramic and **b** the CeZr33-0 min ceramic

306 the tetragonal $I4_1/amd$ symmetry. In fact, this is the only
 307 maximal subgroup of the $Fd\bar{3}m$ group in the tetragonal
 308 system. Transformations of order for cation, anion or both
 309 arrays could justify this reduction in symmetry. For this
 310 new Rietveld refinement, cation occupancies were freely
 311 refined in both 8c and 8d sites, with the only constraint of
 312 full occupancy at each site. This can be justified as long as
 313 the XRD pattern is largely dominated by the scattering of
 314 the heavy cations. For this reason, the same accuracy is not
 315 possible for oxygen atoms, for which we allowed the
 316 possibility of partial occupancy and vacancies in 16g, 8e,
 317 4a and 4b sites but maintained the constraint of global
 318 charge balance. The starting lattice parameters were
 319 obtained with the indexing software TREOR [36] applied
 320 to the first 20 observed pyrochlore reflections. A promising
 321 de Wolff [37] figure of merit $M(20) = 88$ was obtained.

322 Plot of the Rietveld refinement corresponding to the
 323 CeZr16-0 min sintered ceramic is given in Fig. 3a. The
 324 main results of the Rietveld analysis are shown in Table 2.
 325 The major crystalline phase is the Ce-deficient tetragonal
 326 pyrochlore [50.0(4) wt%], with an axial ratio
 327 $c/a\sqrt{2} = 0.989$, highlighting the pseudocubic character of
 328 that tetragonal phase of composition $Zr_{3.21}Ce_{0.78}O_{7.59}$.
 329 Contributions of tetragonal [31.6(2) wt%] and monoclinic

Table 2 Rietveld refinement of the CeZr16-0 min ceramic

Phase	Tetragonal pyrochlore	Tetragonal	Monoclinic	Graphite
Fraction (wt%)	50.0 (4)	31.6 (2)	13.4 (4)	4.9 (2)
a (Å)	7.489 (8)	3.6051 (7)	5.276 (3)	2.413 (3)
b (Å)	7.489 (8)	3.6051 (7)	5.259 (3)	2.413 (3)
c (Å)	10.477 (1)	5.197 (1)	5.165 (3)	6.707 (2)
β	–	–	98.69 (3)	–
Group of symmetry	$I4_1/amd$	$P4_2/nmc$	$P2_1/c$	$P6_3/mmc$
R_{wp}	4.78			
R_{exp}	2.18			
χ^2	4.83			

Table 3 Reliability parameters of the cubic and tetragonal models for the pyrochlore structure

	Cubic pyrochlore	Tetragonal pyrochlore
R_{wp}	5.60	4.78
R_{exp}	2.18	2.18
χ^2	6.6	4.83
R_B	3.7	1.50
R_F	1.97	1.01

Table 4 Rietveld refinement of the CeZr33-0 min ceramic

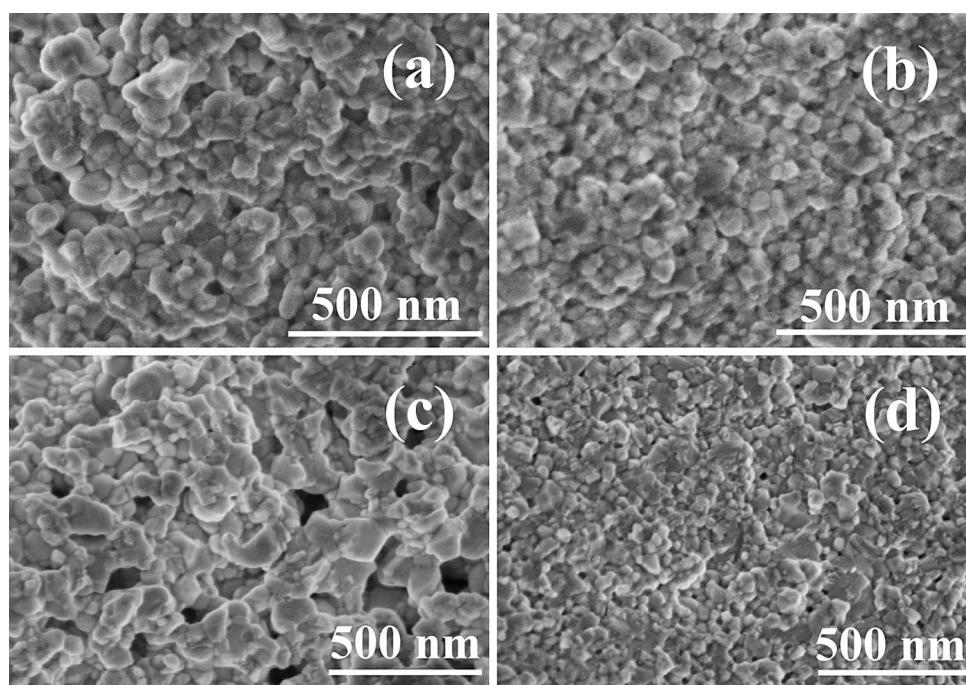
Phase	Tetragonal Pyrochlore	Tetragonal
Fraction (wt%)	81.61 (9)	18.4 (6)
$a = b$ (Å)	7.5115 (9)	3.6100 (6)
c (Å)	10.574 (2)	5.202 (1)
Group of symmetry	$I4_1/amd$	$P4_2/nmc$
R_{wp}	7.32	
R_{exp}	3.67	
χ^2	3.99	

[13.4(4) wt%] phases and a trace of residual graphite [4.9(2) wt%] were also present in the refinement. 330 331

In Table 3, we report the comparison between the reliability parameters for both models, cubic and tetragonal. 332 333 The reported results support the superiority of our tetragonal model. To the best of our knowledge, this is the first 334 335 time that a tetragonal pyrochlore has been reported in the literature for this system. Additional crystallographic data 336 337 for this new structure will be reported elsewhere. 338

The Rietveld analysis for the CeZr33-0 min ceramic 339 was also modeled taking into account the tetragonal variant 340 of the pyrochlore structure just introduced, and the 341

Fig. 4 SEM micrographs of the surface (a) and core (b) area of the CeZr16-0 min ceramic and the surface (c) and core (d) area of the CeZr33-0 min ceramic



342 refinement indicated the formation of only two phases
 343 (Table 4). The major crystalline phase is the Ce-deficient
 344 tetragonal pyrochlore structure [81.6(9) wt%] and the
 345 minor phase the tetragonal one [18.4(6) wt%]. Plot of the
 346 Rietveld refinement corresponding to the CeZr33-0 min
 347 sintered ceramic is given in Fig. 3b. In this case, the
 348 refinement of the occupancy factors led to a composition
 349 $Zr_{2.8}Ce_{1.2}O_{7.4}$ for the pyrochlore structure, and an axial
 350 ratio $c/a\sqrt{2} = 0.995$, also pseudocubic but more distorted
 351 as compared to the previous ceramic.

352 The described phase assemblies are quite different than
 353 the reported ones for the 10 mol% CeO_2-ZrO_2 ceramics
 354 sintered for 5 min and without holding time [17]. In these
 355 cases, whereas in the latter the major crystalline phase is
 356 metastable tetragonal, t' (90.9 wt%), and the minor phase is
 357 tetragonal (9.1 wt%), in the former the phases were
 358 tetragonal (82.5 wt%), monoclinic (15.1 wt%) and py-
 359 rochlore (2.4 wt%). We showed [17] that the obtained
 360 phases are consequence of the highly reducing atmosphere
 361 created by the graphite environment during SPS, which
 362 promotes the reduction of Ce^{4+} ions to Ce^{3+} . However, the
 363 pyrochlore phase was found only when the sintering tem-
 364 perature was held for 5 min. On the contrary, when the
 365 CeO_2 amount increases to 16 and 33 mol%, even when
 366 sintering without holding time the tetragonal phase is
 367 destabilized and great amounts of pyrochlore phase are
 368 present in both ceramics. Also, we have found that the
 369 cubic pyrochlore phase declined into tetragonal pyrochlore.
 370 The reduction of Ce^{4+} ions to Ce^{3+} in the CeZr33-0 min

ceramic promotes also the presence of some porosity in this
 ceramic (Table 1), as a consequence of oxygen loss.

The SEM micrographs of the CeZr16-0 min and
 CeZr33-0 min ceramics are shown in Fig. 4. Fracture
 surface was analyzed in order to avoid possible oxidation
 during polishing and etching. A homogeneous micro-
 structure with a grain size about 50–70 nm in the whole
 ceramic is observed in the CeZr16-0 min ceramic. This
 microstructure is similar to the reported one for the
 CeZr10-0 min ceramic [17]. Conversely, a graded micro-
 structure with 100–150 nm grain size in the edge region
 and 40–70 nm grain size in the core region is observed in
 the CeZr33-0 min ceramic (Table 1). Graded microstruc-
 tures have been previously reported for samples similar to
 the ones under study [27]. During SPS, the edge has much
 lower oxygen partial pressure, which could lead to a gra-
 dient of Ce^{4+} reduction to Ce^{3+} from outside to inside.
 Whereas for the CeZr16-0 min ceramic it is thought that
 most of the Ce^{4+} has converted to Ce^{3+} according to the
 homogeneous microstructure, for the CeZr33-0 min it
 looks like the reduction beneath the edge area was not as
 fast and complete as that of the edge area, giving rise to the
 graded microstructure.

Nyquist plots measured on the CeZr10-0 min and
 CeZr33-0 min ceramics at 600 °C are shown in Fig. 5.
 These compositions have been selected on the basis of their
 Ce content. The spectra obtained have been fitted to an
 equivalent circuit composed by two RQs (constant phase
 element in parallel with a resistance) connected in series

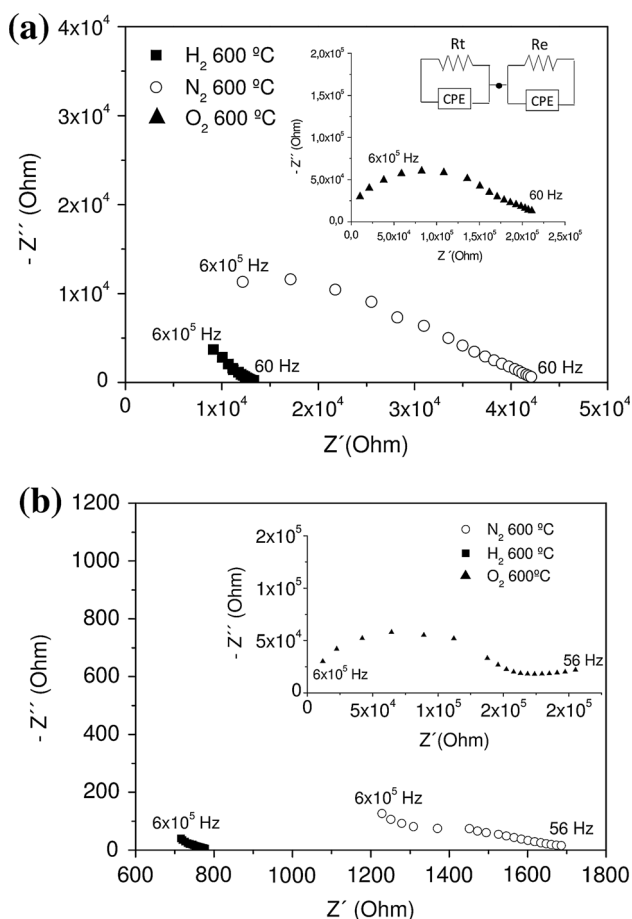


Fig. 5 Nyquist plots of the **a** CeZr10-0 min and **b** CeZr33-0 min ceramics, measured in N_2 , H_2 and O_2 atmospheres at 600 °C

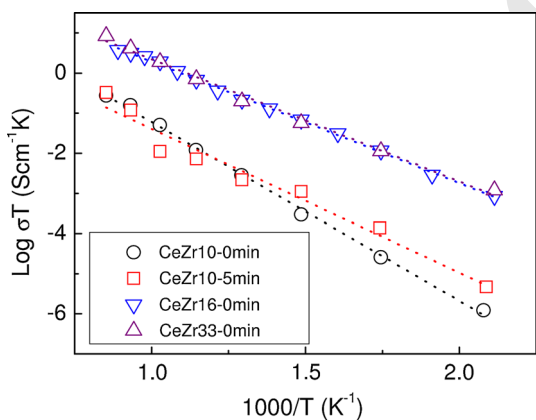


Fig. 6 Electrical conductivity versus temperature measured in the sintered ceramics in nitrogen atmosphere

400 (inset in Fig. 5a). The first one has been ascribed to the
 401 material, while the second one is related to the interface
 402 between the electrode and the ceramic sample. On this
 403 sense, the conductivity has been calculated from intercept

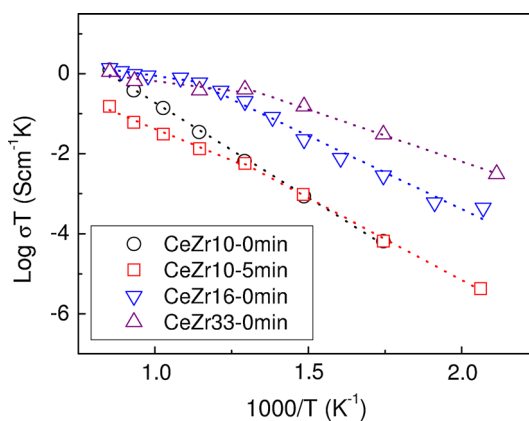


Fig. 7 Electrical conductivity versus temperature measured in the sintered ceramics in hydrogen atmosphere

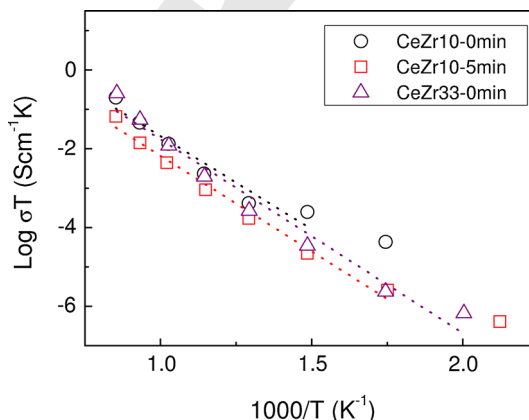


Fig. 8 Electrical conductivity versus temperature measured in the sintered ceramics in oxygen atmosphere

of the first semicircle with the real part of impedance. This
 value represents the total conductivity of the material,
 while the arc corresponding to the ceramic–electrode
 interface was not analyzed in this work.

Figures 6, 7 and 8 show the Arrhenius plots for all the
 studied ceramics measured in N_2 , H_2 and O_2 atmosphere,
 respectively. The slope of these diagrams has been used
 to calculate the activation energy of the conducting species
 (Table 5).

It is clear that the Arrhenius plots are highly dependent
 on the ceramic phase assembly. In the CeZr10-0 min
 ceramic (metastable t' phase: 91 wt%, tetragonal phase:
 9 wt% [17]), single activation energies were evidenced
 for the whole temperature range in the three different at-
 mospheres, pointing out to the existence of only one con-
 duction mechanism. A value close to 0.85 eV was obtained
 in the three cases, very similar to the reported one by
 previous authors [5, 6, 8] for ceramics with similar

404
 405
 406
 407
 408
 409
 410
 411
 412
 413
 414
 415
 416
 417
 418
 419
 420
 421

Table 5 Phase assembly and electrical properties of the sintered ceramics

Ceramic	Phases from Rietveld refinement (wt%)	E_a (eV)			
		N ₂ atmosphere	H ₂ atmosphere		O ₂ atmosphere
			200–500 °C	500–900 °C	
CeZr10-0 min	t' 90.9 %, t 9.1 %	0.85	0.90		0.90
CeZr10-5 min	t 82.5 %, m 15.1 %, p 2.4 %	0.68	0.78	0.60	0.92
CeZr16-0 min	t 31.6 %, m 13.4 %, p 50.0 %	0.58	0.70	0.20	–
CeZr33-0 min	t 18.4 %, p 81.6 %	0.58	0.49	0.18	0.93

422 composition and phases, and equilibrium defect concen-
423 trations. This result is consistent with the activation energy
424 for oxygen vacancy conduction in zirconia-based ceramic
425 oxides [5, 6], where the electronic contribution to the total
426 conductivity is not significant comparing with the ionic.
427 The lower value of conductivity was registered when
428 measuring in the O₂ atmosphere. This is consequence of
429 the re-oxidation of the Ce³⁺ ions to Ce⁴⁺, which eliminates
430 the electronic conductivity of the samples.

431 In the CeZr10-5 min, CeZr16-0 min and CeZr33-0 min
432 ceramics, with more complex phase assemblies, different
433 behavior was obtained as a function of the present phases
434 and also as a function of the measuring atmosphere. Dif-
435 ferences were observed in the activation energies as a
436 function of the amount of pyrochlore phase in these
437 ceramics, when the conductivity was measured in N₂
438 (Table 5). In the two ceramics showing a high amount of
439 pyrochlore, activation energy of 0.58 eV was obtained.
440 This value is very similar to the reported one by Baidya
441 et al. [14] for the Ce₂Zr₂O₇ phase, which is shown to be an
442 n-type semiconductor in the temperature range 400–850 K.
443 Thus, we can conclude that the pyrochlore phase is con-
444 trolling the conducting behavior in these two ceramics. In
445 the CeZr10-5 min ceramic, with only a 2.40 wt% pyroch-
446 lore phase, an activation energy of 0.68 eV was found,
447 which is an intermediate value between the corresponding
448 one for oxygen vacancy conduction (0.85 eV) and the
449 corresponding one for n-type conduction (0.5 eV). In this
450 ceramic, the low percentage of pyrochlore can significantly
451 modify the conducting behavior of the material.

452 It is noticeable that whereas the Arrhenius plots obtained
453 in N₂ and O₂ were straight lines, a slope change was
454 noticed around 500 °C when measuring the conductivity in
455 H₂ atmosphere. In the CeZr10-5 min ceramic, the activa-
456 tion energy decreases from 0.78 to 0.60 eV. In the CeZr16-
457 0 min and CeZr33-0 min ceramics, the observed decrease
458 in activation energy is more significant, with values of
459 0.18–0.20 eV in the high temperature range (500–900 °C).

460 The changes in the Arrhenius plots slope have been usu-
461 ally related to changes in physical or chemical structure or to
462 the existence of two conduction mechanisms [5, 6].

463 Temperature programmed reduction (TPR) studies carried
464 out by different authors in the CeO₂–ZrO₂ system [14, 23]
465 have shown the existence of two peaks around 450–550 and
466 700–800 °C on the hydrogen uptake for Ce_xZr_{1-x}O₂ reduc-
467 tion. The oxygen stoichiometries estimated from the quantity
468 of hydrogen uptake showed that the first step reduction
469 corresponds to Ce₂Zr₂O₇ (pyrochlore I) and the second step
470 reduction corresponds to Ce₂Zr₂O_{6.2} (pyrochlore II) [14].

471 Taking these reports into account, the decrease in slope
472 in the high temperature range described above may be
473 clarified. In the ceramic with initially only 2.40 wt% py-
474 rochlore phase, a higher degree of reduction could be
475 achieved during the conductivity measurement in H₂
476 atmosphere, which resulted in a structural change into a
477 higher amount of pyrochlore. Thus, an activation energy
478 corresponding to n-type conduction was obtained in this
479 ceramic. In the CeZr16-0 min and CeZr33-0 min ceramics,
480 the pyrochlore amounts were initially 50.0 and 81.6 wt%,
481 respectively. Thus, during the conductivity measurement in
482 the highly reducing atmosphere, the pyrochlore I could be
483 strongly reduced into Ce₂Zr₂O_{6.2}. This phase has been
484 shown to have a significantly low resistivity, which
485 remains constant in the 400–1000 K range [14]. Activation
486 energy of 0.08 eV was reported for lower temperatures.
487 Thus, the low activation energies found in the CeZr16-
488 0 min and CeZr33-0 min ceramics are clearly related to the
489 presence of Ce₂Zr₂O_{6.2} phase.

490 Regarding the conductivity values, higher values were
491 obtained in the CeZr16-0 min and CeZr33-0 min ceramics
492 in the whole range of temperature, when measuring in N₂
493 and H₂ atmosphere. This is clearly related to the presence
494 of pyrochlore in the ceramics.

495 When characterizing the ceramics in O₂ atmosphere,
496 very similar Arrhenius plots were found in all of them.
497 Activation energy ~0.9 eV was found in all the ceramics;
498 thus, the electrical conductivity shows the typical ionic
499 conduction behavior, and the oxygen anti-Frenkel defects
500 are the predominant defects. It is clear that the re-oxidation
501 of the ceramics promoted a decrease in the concentration of
502 oxygen vacancies, as the lower conductivity values were
503 obtained when measuring in O₂ atmosphere.

504 **Conclusions**

505 Spark plasma sintering of $Ce_xZr_{1-x}O_2$ ($x = 0.10, 0.16$ and
506 0.33) powders obtained by a two-step synthesis technique
507 resulted in ceramics with different phase assemblies, as a
508 consequence of the reduction of Ce^{4+} to Ce^{3+} in the highly
509 reducing atmosphere created by the graphite environment
510 during the sintering process. Phase identification carried
511 out by means of Rietveld refinements showed the presence
512 of a Ce-deficient tetragonal pyrochlore as the major phase
513 in the ceramics with higher CeO_2 content, with tetragonal
514 and monoclinic as minor phases.

515 The electrical conductivity of the ceramics was highly
516 dependent on the phase assembly, and higher conductivity
517 values were obtained in the ceramics with higher pyrochlore
518 content, when measuring in N_2 and H_2 atmosphere.
519 Whereas the ceramics with tetragonal phase showed an
520 ionic conduction by oxygen vacancies independent of the
521 atmosphere, a significant effect of the measuring atmosphere
522 was observed in the ceramics with pyrochlore
523 phase. A n-type semiconducting behavior seems to manage
524 the conduction mechanism in the latter when measuring in
525 N_2 . However, a significant decrease in the activation
526 energy was noticed around $500\text{ }^\circ\text{C}$ when measuring the
527 conductivity in H_2 atmosphere, consequence of the strong
528 reduction promoted in these ceramics during the mea-
529 surement. However, similar activation energies were
530 observed for all compositions measured in O_2 , which cor-
531 responds to ionic conduction behavior reported in the
532 literature.

533 **Acknowledgements** Dr. Cruz thanks Junta de Andalucía (TEP-
534 1048) for her fellowship. The financial support for this work has been
535 obtained from the Spanish Ministerio de Ciencia e Innovación
536 (ENE2009-14522-C05-01) and (ENE2009-14522-C05-03). Cofi-
537 nanced by FEDER funds from the European Union and from Junta de
538 Andalucía (P09-TEP-5454).

539 **References**

- 540 1. Kaspar J, Fornasiero P, Graziani M (1999) Use of CeO_2 -based
541 oxides in the three-way catalysis. *Catal Today* 50(2):285–298
- 542 2. Trovarelli A (2002) Catalysis by ceria and related materials.
543 Imperial College press, London
- 544 3. Fergus JW (2006) Oxide anode materials for solid oxide fuel
545 cells. *Solid State Ion* 177(17–18):1529–1541
- 546 4. Boaro M, Vicario M, Llorca J, de Leitenburg C, Dolcetti G,
547 Trovarelli A (2009) A comparative study of water gas shift
548 reaction over gold and platinum supported on ZrO_2 and CeO_2 -
549 ZrO_2 . *Appl Catal B Environ* 88(3–4):272–282
- 550 5. Reidy RF, Simkovich G (1993) Electrical conductivity and point
551 defect behavior in ceria-stabilized zirconia. *Solid State Ion*
552 62(1–2):85–97
- 553 6. Chiodelli G, Flor G, Scagliotti M (1996) Electrical properties of
554 the ZrO_2 - CeO_2 system. *Solid State Ion* 91(1–2):109–121

7. Boaro M, Trovarelli A, Hwang JH, Mason TO (2002) Electrical
555 and oxygen storage/release properties of nanocrystalline ceria-
556 zirconia solid solutions. *Solid State Ion* 147(1–2):85–95
- 557 8. Lee JH, Yoon SM, Kim BK, Lee HW, Song HS (2002) Electrical
558 conductivity and defect structure of CeO_2 - ZrO_2 mixed oxide.
559 *J Mater Sci* 37(6):1165–1171
- 560 9. Lee JH, Yoon SM, Kim BK, Kim J, Lee HW, Song HS (2001)
561 Electrical conductivity and defect structure of yttria-doped ceria-
562 stabilized zirconia. *Solid State Ion* 144(1–2):175–184
- 563 10. Shannon RD (1976) Revised effective ionic radii and systematic
564 studies of interatomic distances in halides and chalcogenides.
565 *Acta Cryst A* 32:751–767
- 566 11. Otake T, Yugami H, Naito H, Kawamura K, Kawada T, Mizusaki J
567 (2000) Ce^{3+} concentration in ZrO_2 - CeO_2 - Y_2O_3 system studied by
568 electronic Raman scattering. *Solid State Ion* 135(1–4):663–667
- 569 12. Huang S, Li L, Van der Biest O, Vleugels J (2005) Influence of
570 the oxygen partial pressure on the reduction of CeO_2 and CeO_2 -
571 ZrO_2 ceramics. *Solid State Sci* 7(5):539–544
- 572 13. Belous AG, Kravchik KV, Pashkova EV, Bohnke O, Galven C
573 (2007) Influence of the chemical composition on structural
574 properties and electrical conductivity of Y-Ce-Zr O_2 . *Chem*
575 *Mater* 19(21):5179–5184
- 576 14. Baidya T, Hegde MS, Gopalakrishnan J (2007) Oxygen-release/
577 storage properties of $Ce_{0.5}M_{0.5}O_2$ (M=Zr, Hf) oxides: interplay of
578 crystal chemistry and electronic structure. *J Phys Chem B*
579 111(19):5149–5154
- 580 15. Song SD, Fuentes RO, Baker RT (2010) Nanoparticulate ceria-
581 zirconia anode materials for intermediate temperature solid oxide
582 fuel cells using hydrocarbon fuels. *J Mater Chem* 20(43):9760–9769
- 583 16. Boaro M, Desinan S, Abate C, Ferluga M, de Leitenburg C,
584 Trovarelli A (2001) Study on redox, structural and electrical
585 properties of $Ce_xZr_{1-x}O_2$ for applications in SOFC anodes.
586 *J Electrochem Soc* 158(2):22–29
- 587 17. Cruz SA, Poyato R, Cumbreira FL, Odriozola JA (2012) Nano-
588 structured spark plasma sintered Ce-TZP ceramics. *J Am Ceram*
589 *Soc* 95(3):901–906
- 590 18. Omori M (2000) Sintering, consolidation, reaction and crystal
591 growth by the spark plasma system (SPS). *Mat Sci Eng A*
592 287:183–188
- 593 19. Munir ZA, Anselmi-Tamburini U, Ohyanagi M (2006) The effect
594 of electric field and pressure on the synthesis and consolidation of
595 materials: a review of the spark plasma sintering method. *J Mater*
596 *Sci* 41(3):763–777
- 597 20. Anselmi-Tamburini U, Garay JE, Munir ZA (2006) Fast low-
598 temperature consolidation of bulk nanometric ceramic materials.
599 *Scr Mater* 54(5):823–828
- 600 21. Omata T, Kishimoto H, Otsuka-Yao-Matsuo S, Ohtori N, Ume-
601 saki N (1999) Vibrational spectroscopic and X-ray diffraction
602 studies of cerium zirconium oxides with Ce/Zr composition
603 ratio = 1 prepared by reduction and successive oxidation of t' -
604 ($Ce_{0.5}Zr_{0.5}O_2$) phase. *J Solid State Chem* 147(2):573–583
- 605 22. Hui Z, Nicolas G, Françoise V, Michele P (2003) Preparation and
606 electrical properties of a pyrochlore-related $Ce_2Zr_2O_{8-x}$ phase.
607 *Solid State Ion* 160(3–4):317–326
- 608 23. Ouyang J, Yang HM (2009) Investigation of the oxygen exchange
609 property and oxygen storage capacity of $Ce_xZr_{1-x}O_2$ nanocrystals.
610 *J Phys Chem C* 113(17):6921–6928
- 611 24. Leonov AI, Andreeva AB, Keler EK (1966) Influence of the gas
612 atmosphere on the reaction of zirconium dioxide with oxides of
613 cerium. *Izq Akad Nauk SSSR Neorganicheskie Mater* 2:137–144
- 614 25. Rodriguez-Carvajal J (1990) FULLPROF: a program for Rietveld
615 refinement and pattern matching analysis. In: Abstracts of the
616 satellite meeting on powder diffraction of the XV congress of the
617 IUCr, pp 127–130
- 618 26. Ortiz AL, Sánchez-Bajo F, Padture NP, Cumbreira FL, Guiberteau F
619 (2001) Quantitative polytype-composition analyses of SiC using
620

- 621 X-ray diffraction: a critical comparison between the polymorphic
622 and the Rietveld methods. *J Eur Ceram Soc* 21:1237–1248
- 623 27. Caglioti G, Paoletti A, Ricci FP (1958) Choice of collimators for a
624 crystal spectrometer for neutron diffraction. *Nucl Inst* 3:223–228
- 625 28. Pecharsky VK, Zavalij PY (2009) *Fundamentals of powder dif-*
626 *fraction and structural characterization of materials*, 2nd edn.
627 Springer, Berlin
- 628 29. Kaspar J, Formagiero P (2002) Structural properties and thermal
629 stability of ceria-zirconia and related materials. In: Trovarelli A
630 (ed) *Catalysis by ceria and related materials*. Imperial College
631 press, London, pp 217–241
- 632 30. Huang SG, Van der Biest O, Vleugels J, Vanmeensel K, Li L
633 (2007) Characterization of Y_2O_3 , CeO_2 and $Y_2O_2 + CeO_2$ FGM
634 tetragonal ZrO_2 ceramics by spark plasma sintering. *Key Eng*
635 *Mater* 333:231–234
- 636 31. Thomson JB, Armstrong AR, Bruce PG (1999) An oxygen-rich
637 pyrochlore with fluorite composition. *J Solid State Chem*
638 148:56–62
32. Sasaki T, Ukyo Y, Kuroda K, Arai S, Muto S, Saka H (2004) 639
Crystal structure of $Ce_2Zr_2O_7$ and $\beta-Ce_2Zr_2O_{7.5}$. *J Ceram Soc Jpn*
640 112:440–444
33. Kishimoto H, Omata T, Otsuka-Yao-Matsuo S, Ueda K, Hosono 641
H, Kawazoe H (2000) Crystal structure of metastable $\kappa-CeZrO_4$
642 phase possessing an ordered arrangement of Ce and Zr ions.
643 *J Alloys Compd* 312:94–103
34. Thornber MR, Bevan DJM, Graham J (1968) Mixed oxides of the 644
type $MO_2(\text{fluorite})-M_2O_3$. III. Crystal structures of the interme-
645 diate phases $Zr_5Sc_2O_{13}$ and $Zr_3Sc_4O_{12}$. *Act Cryst B* 24:1183–1190
35. Wuensch BJ, Eberman KW (2000) Order-disorder phenomena in 646
 $A_2B_2O_7$ pyrochlore oxides. *J Metals* 52:19–21
36. Werner PE, Erikson L, Westdahl M (1985) *TREOR*, a semi- 647
exhaustive trial-and-error powder indexing program for all
648 symmetries. *J Appl Cryst* 18:367–370
37. de Wolff PM (1968) A simplified criterion for the reliability of a 649
powder pattern indexing. *J Appl Cryst* 1:108–113
- 650
651
652
653
654
655
656

UNCORRECTED PROOF