ELSEVIER

Ceramics International 33 (2007) 471–475

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Rapid densification by using Bi_2O_3 as an aid for sintering of gadolinia-doped ceria ceramics

V. Gil *, J. Tartaj, C. Moure, P. Duran

Instituto de Cerámica y Vidrio (CSIC), Campus de Cantoblanco, Kelsen 5, Cantoblanco, Madrid 28049, Spain

Received 31 May 2005; received in revised form 8 October 2005; accepted 25 October 2005
Available online 19 January 2006

Abstract

Densification process and microstructure development in Bi_2O_3-doped gadolinia ceria (GDC) submicrometer powders have been studied by the constant heating rate (CHR) method in air and by SEM observations. Densification of GDC was strongly enhanced by adding small amounts of Bi_2O_3, and samples of GDC containing $\leq$1 wt% Bi_2O_3 sintered at 1200–1400 °C for 2 to 4 h were near theoretically dense bodies (98–99.8% of theoretical), i.e., about 250–300 °C lower than that for undoped-GDC ceramics. A transient liquid phase-assisting mechanism was assumed to be the main cause for such an improvement. The grain size of GDC ceramics was hardly affected by the Bi_2O_3 additions during sintering. A total electrical conductivity as high as 4 S m^{-1} at 700 °C for the doped-GDC samples sintered at 1400 °C, was measured.
© 2005 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: A. Sintering; A. Grain growth; C. Electrical conductivity; CeO_2–Gd_2O_3; Bi_2O_3 doping

1. Introduction

Yttria stabilized zirconia (YSZ), exhibiting a sufficiently high ionic conductivity is the state-of-the-art material for conventional solid oxide fuel cells (SOFCs) which operate in the temperature range of 900–1000 °C [1]. However, these thermal operating conditions require too expensive materials for the other structural SOFC components, i.e., anode, cathode, interconnectors, and heat exchangers, making the fabrication cost prohibitive as well as it is detrimental to the efficiency of the fuel for wide commercial applications. Therefore, the need for the development of SOFCs operating at lower temperature is a very important challenge to be achieved. Among other reasons, lower operating temperature would favour the use of less expensive structural components as, for example, metallic interconnects instead of the Cr-containing ceramic interconnects. It also would reduces the materials degradation increasing, thus, the long-term stability of the SOFC.

Among the components of SOFC, the electrolyte is the most critical and, therefore, the major research efforts have been made in the search of an alternative electrolyte which should possess the same or higher ionic conductivity in the temperature range of 500–700 °C, as that of the YSZ at 1000 °C. The electrolyte of choice has been ceria-based ceramics which have been shown to exhibit four to five times higher ionic conductivity than YSZ at intermediate temperatures [2–4]. However, some problems arising from ceria-based electrolytes for SOFCs will have to be resolved before its use as the only or the best candidate. Among them the most important are the following: (i) ceria-based electrolytes are known to be reduced at low oxygen partial pressure and, therefore, they will exhibit electronic conductivity and a certain expansion as consequence of the Ce^{4+} to Ce^{3+} reduction, and (ii) another problem, if not the most important, is that ceria-based electrolyte requires sintering temperatures to full density in the range of 1350–1600 °C, resulting in microstructures with grain size too large to be mechanically stable at the operating conditions of the SOFCs. This difficulty hinders the use of ceria-based electrolyte in SOFC applications [5–7].

Although limited, some processing alternatives can be used to overcome the above mentioned difficulties. One of them would be the use of nanosized GDC ceramic powders as raw material which are sinterable at low-temperature, however the price of these materials are almost prohibitive to be used in an on line fabrication process of SOFC components. Another alternative would be the use of a less expensive commercial

* Corresponding author. Tel.: +34 91 735 58 40; fax: +34 91 735 58 43.
E-mail address: vanesa@icv.csic.es (V. Gil).

0272-8842/$32.00 © 2005 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2005.10.012

GDC raw material, and to lower the sintering temperature by means of using sintering aids. It is this second alternative that we propose as the aim and objective in the present paper. To do that we choose Bi_2O_3 as the sintering aid to lower the sintering temperature of GDC ceramics, and their influence on the crystalline structure, densification behavior, grain growth and electrical conductivity are advanced in this communication.

2. Experimental procedure

As raw material a commercial $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) submicronized powder (Rhodia) characterized by a specific surface area of 12.4 m^2/g and an average particle size of 0.38 μm, has been used. The dopant (0.2–10 wt% Bi_2O_3), in the form of bismuth nitrate dissolved in ethanol was added to a GDC powder/ethanol suspension by stirring. After drying at 120 °C for 2 h, the powders were calcined at 700 °C for 2 h, granulated and isopressed at 200 MPa. After compaction the sintering was performed at a constant heating rate (CHR) of 2 °C/min up to 1600 °C in a Netzsch dilatometer (model 407/E of Geratebau, Bayern, Germany). The samples were also isothermally sintered in air at several temperatures for sintering time of 0–8 h at a heating rate of 2 °C/min and a cooling rate of 5 °C/min. The density of the samples was measured by the Archimedes method in water.

The influence of the bismuth oxide additive on the crystalline structure of the prepared samples was studied by X-ray diffraction on the samples heat-treated at the 1200–1400 °C temperature range and milled in an agate mortar. The characterization was carried out with a X-ray diffractometer Siemens (model D-5000, Erlangen, Germany) with nickel-filtered Cu Kα radiation (λ = 0.15405 nm). For the lattice parameter measurements, alumina as an internal standard was used. An average value obtained from three samples was taken and the deviation was ±0.0005 Å. The microstructure of the sintered samples was examined in a Zeiss (SEM) scanning electron microscope (model DSM 950, Oberkochem, Germany). The average grain size was measured by the line intercept method on the surface of polished and thermally etched sintered samples. The size of at least 300 grains was taken into account and the deviation was ±10% of the measured value.

The total electrical conductivity of the dense Bi_2O_3-doped GDC samples was measured in the temperature range of 200–700 °C at a fixed frequency of 10 kHz. Silver paint was backed onto each side of the sintered samples at 750 °C for 1 h, to ensure good contact with the samples. Platinum wires attached to the electrode provided current contacts to each electrode on the sintered samples.

3. Results and discussion

Fig. 1 shows the XRD pattern of Bi_2O_3-doped and undoped-GDC powders heat-treated at 1200 °C for 2 h. There are no new peaks identifiable in the patterns, indicating that there is no reaction between Bi_2O_3 and GDC or if some secondary phase

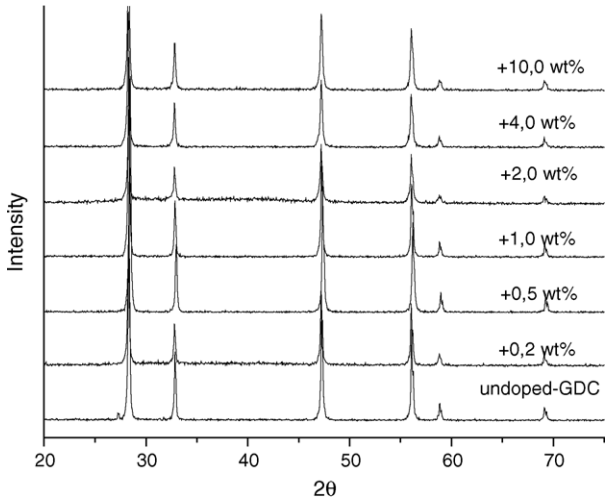

Fig. 1. XRD patterns of GDC samples doped with different Bi_2O_3 contents.

was formed the amount was too small to be detected by X-ray diffraction. Hrovat et al. [8] found that Bi_2O_3 is soluble in CeO_2 forming a cubic fluorite solid solution $Bi_{1-x}Ce_xO_{2-x/2}$ and the solid solubility of CeO_2 in Bi_2O_3 is not observed. However, when using Bi_2O_3 as a sintering aid to lower sintering temperature of the YSZ electrolyte, some reaction between them was detected and the YSZ structure deteriorated [9,10]. Although it is not shown here, it was found that the unit-cell parameters of the GDC cubic solid solution increases steadily with increasing bismuth content up to about 1 wt%, and then remained constant for higher Bi_2O_3 concentration. Such an increase of the cubic unit-cell can be considered to be due to the substitution of the larger Bi^{3+} ions (0.117 nm) for the smaller Ce^{4+} ions (0.097 nm) [11]. From our experimental results, we estimated that the maximum of Bi_2O_3 to be dissolved in the cubic GDC structure or, in other words, the solid solubility limit of Bi_2O_3 in gadolinia-doped ceria was 0.8 wt% in the temperature range of 1200–1400 °C. This result is in contrast with those of Keizer and Burggraaf [10], where they found that Bi_2O_3 dissolved up to about 2 wt% in the cubic YSZ structure.

The shrinkage rate spectra of GDC samples doped with concentrations of Bi_2O_3 >0.5 wt% showed a pronounced peak while that of the samples containing lower contents of Bi_2O_3 ≤0.5 wt% are somewhat broader, indicating a more gradual densification. Fig. 2 shows typical shrinkage rate spectra of undoped and GDC samples doped with 0.5 and 2 wt% Bi_2O_3. The effect of Bi_2O_3 additions in lowering the T_s, i.e., the temperature at which the density of the sintered sample attains ≥95% theoretical density, was of the order of almost 200 °C in the case of the 0.5 wt% Bi_2O_3, and as high as almost 300 °C when the additive content was 2 wt% in a non-isothermal sintering process. The width of the shrinkage rate temperature range rapidly decreases and already for the 1 wt% Bi_2O_3 was much narrower. Such a behavior is characteristic of a liquid phase-assisted sintering. These results suggest that Bi_2O_3 additions dramatically reduce the sintering temperature of GDC ceramics, and this can be related with the formation of a

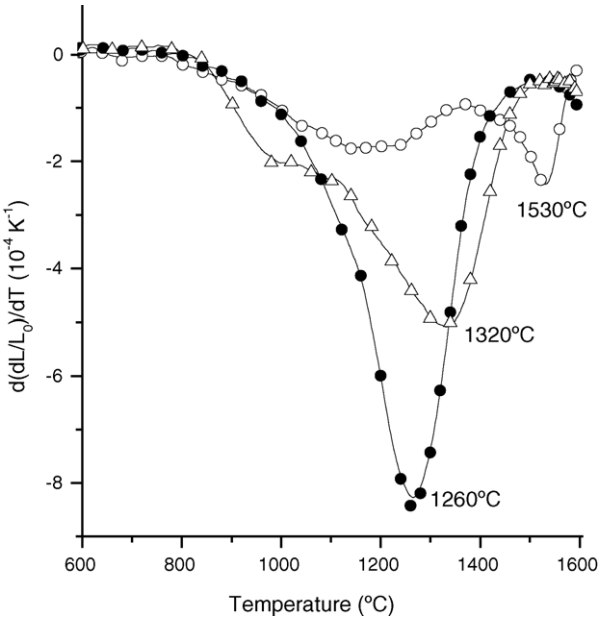

Fig. 2. Shrinkage rate spectra of undoped-GDC samples (○), 0.5 wt% Bi_2O_3 (△), and 2 wt% Bi_2O_3 (●) doped-GDC samples.

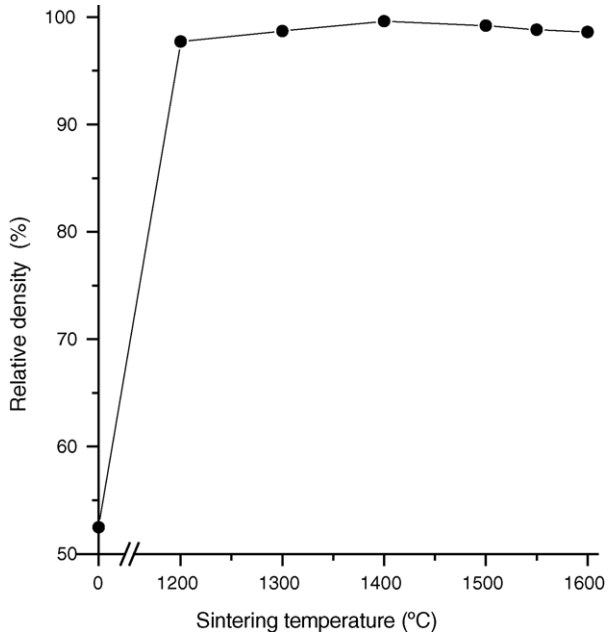

Fig. 3. Relative density for 1 wt% Bi_2O_3-doped GDC sintered at 1200–1600 °C for 4 h.

transient (fugitive) liquid phase as consequence of the melting of the Bi_2O_3 at or below 820 °C. It must be mentioned that the density of the sintered GDC ceramics deteriorated above 1350–1400 °C, i.e., a dedensification phenomenon is to exist when the Bi_2O_3 content was higher than 1 wt%, which can be due to both a rapid volatilization of Bi_2O_3 and/or the evolution of oxygen gas produced as consequence of some reduction of Ce^{4+} to Ce^{3+} [12].

Fig. 3 shows the effect of 1 wt% Bi_2O_3 addition on the sintering behavior of GDC ceramics as a function of the temperature for a holding time of 4 h. As it can be seen, sintering at 1200 °C achieved a density of about 98% of

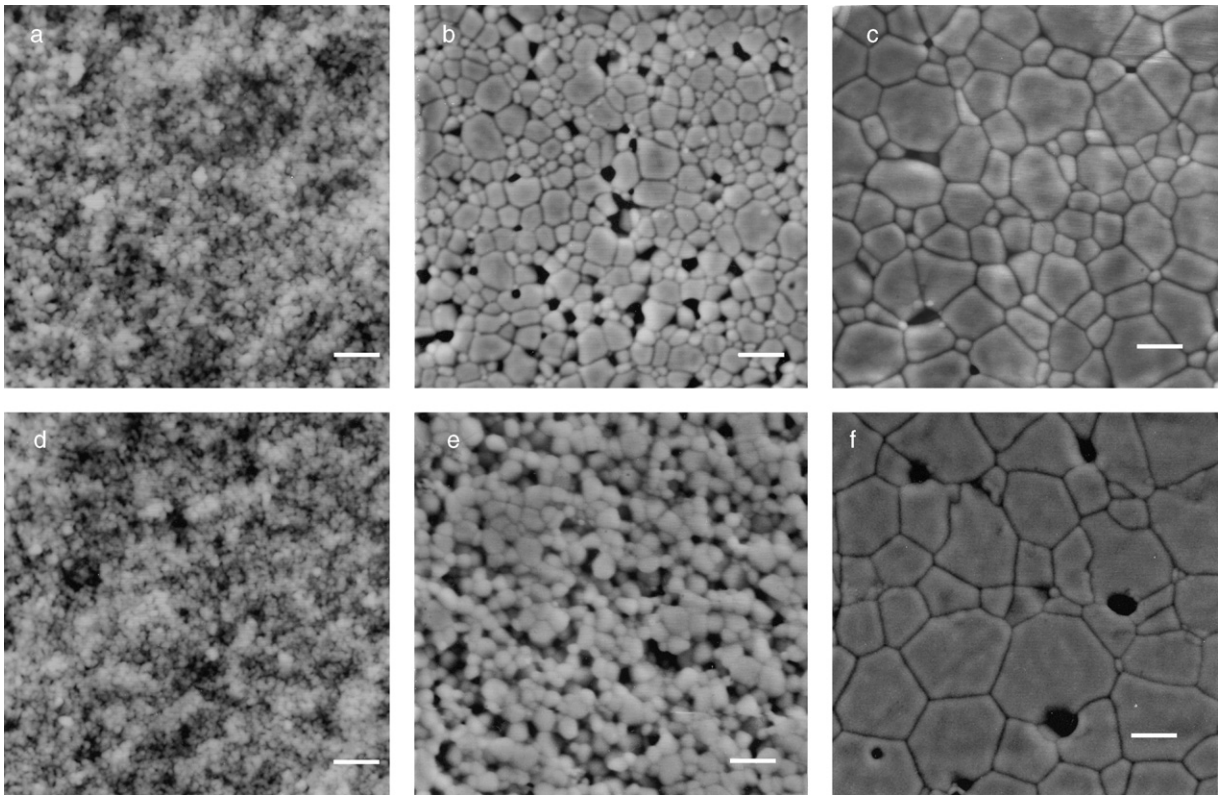

Fig. 4. SEM micrographs of undoped-(a–c) and 1 wt% Bi_2O_3-doped GDC (d–f) sintered samples (bar = 2 μm).

theoretical and, for example, at 1400 °C the density was 99.6% of theoretical, i.e., completion of sintering within a relatively short range of temperature can be reached by using Bi_2O_3 as a sintering aid for gadolinia-doped ceria ceramics. A temperature range between 1300 and 1400 °C, can be considered as a very competitive temperature for a co-sintering process, when necessary, for the different SOFCs components together [1].

Fig. 4 shows SEM images of undoped-GDC samples sintered at 1200, 1400, and 1550 °C and GDC samples containing 1 wt% Bi_2O_3. As it can be seen, the undoped-GDC samples sintered at 1200 and 1400 showed many pores, and it is only well sintered with few closed pores and relatively uniform grain size distribution when sintered at 1550 °C. By comparison, the GDC sintered samples containing 1 wt% Bi_2O_3 had smaller grains than undoped-GDC and were much denser with a few pores located at the grain boundaries, i.e., the grain-boundary mobility was decreased by Bi_2O_3 addition, which indicates a probable inhibitor role in the grain growth process.

Fig. 5 shows the variations in the average grain size of GDC samples doped with 1 wt% Bi_2O_3 as a function of the sintering temperature. By comparison, in the same figure is also plotted for those corresponding to the undoped-GDC samples. As it can be seen, the Bi_2O_3 addition hardly influences the grain growth, rather retard or at least do no promotes it. The average grain size was always somewhat smaller in the doped-GDC samples sintered in the temperature range of 1000–1600 °C for a holding time of 2 h. From that figure it seems to be that there are three well established regions, one of them up to 1200 °C in which no grain growth takes place. The second one between 1200 and 1400 °C in which a moderate grain growth occurs and, finally, a third region above 1400 °C in which a rapid grain growth took place.

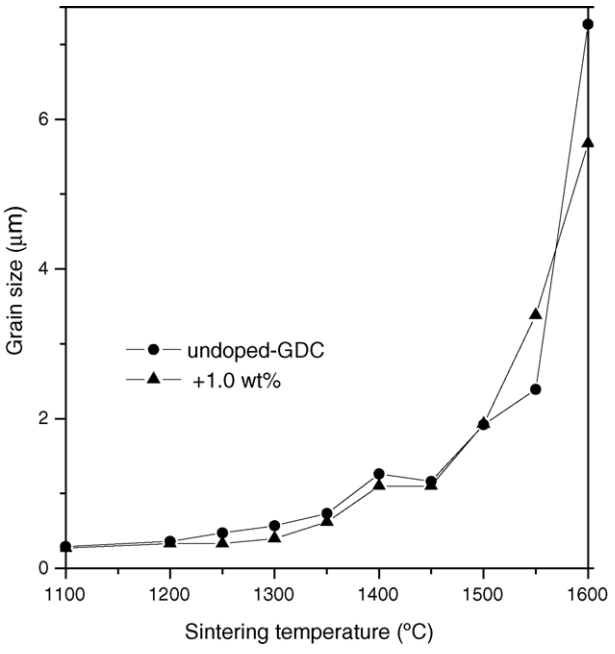

Fig. 5. Variation in measured grain size for undoped- and 1 wt% Bi_2O_3-doped GDC samples with sintering temperature.

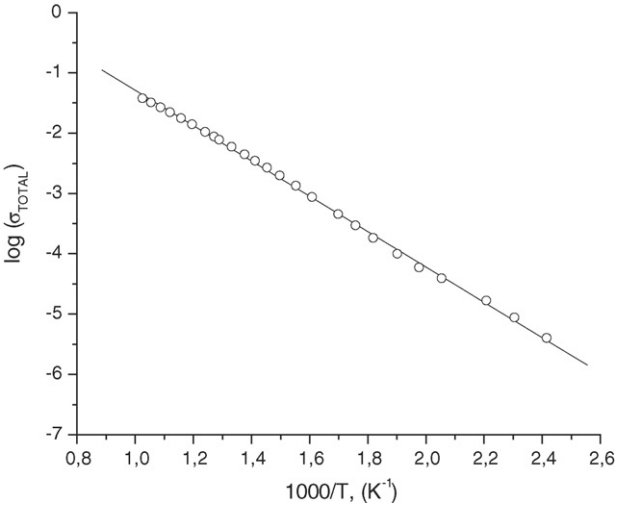

Fig. 6. Arrhenius plots for 1 wt% Bi_2O_3-doped GDC samples sintered at 1400 °C for 2 h.

Temperature dependence of electrical conductivity of the GDC samples doped with 1 wt% Bi_2O_3 sintered at 1400 °C for 2 h as a function of the temperature is shown in Fig. 6. The electrical conductivity increased with temperature to 4 S m^{-1} at 700 °C, which is very slightly lower than that of the undoped-GDC sample measured at the same temperature, 4.1 S m^{-1}. Some negative influence of the residual liquid phase remaining at the triple point of the microstructure in the doped-GDC sintered samples could be the cause for the slight decrease in the total conductivity. Besides this, the smaller grain size of the doped-GDC samples and, therefore, with a higher grain-boundary density could also negatively affect the electrical conductivity. From the Arrhenius plots shown in the above figure, an activation energy of 0.77 eV was calculated which is slightly lower than that for undoped-GDC samples (≈0.80 eV) indicating, thus, an easier migration of the oxygen-ion vacancies through the cleaner grain-to-grain contacts in the microstructure of the Bi_2O_3-doped GDC samples. Although it is not clear, a certain scavenger role of the additive during sintering, similarly to that attributed for Fe_2O_3 when used as a sintering aid of GDC ceramics [13], could be assumed.

4. Conclusions

From all the above described results we can summarize as follows, (i) Bi_2O_3 has a noticeable influence in reducing the sintering temperature, between 200 and 300 °C, of GDC ceramics. Such densification enhancement is assumed to take place via a transient liquid phase-assisting mechanism, (ii) Bi_2O_3 dissolves in the cubic GDC structure in up to 0.8 wt% in the temperature range of 1200–1400 °C, (iii) Bi_2O_3 additions (0.2–2 wt%) causes, in the present experimental conditions, the development of a normal microstructure and do not promote grain growth during sintering of doped-GDC ceramics and, (iv) GDC ceramics doped with 1 wt% Bi_2O_3 and sintered at 1400 °C for 2 h had a smaller grain size than the undoped-GDC samples and a similar total electrical conductivity, 4.0 S m^{-1} against 4.1 S m^{-1}, at 700 °C.

Acknowledgements

The present work was financed by the Spanish CICYT under Project CICYT. MAT 2003-0111163 and a grant from the Autonomous Community of Madrid.

References

[1] N.Q. Minh, Ceramic fuel cells, J. Am. Ceram. Soc. 76 (1993) 563–588.
[2] T.S. Etsell, S.N. Flengas, The electrical properties of solid oxide electrolytes, Chem. Rev. 70 (1970) 339–376.
[3] G.S. Lewis, A. Atkinson, B.C.H. Steele, Sintering of gadolinia-doped ceria at reduced temperatures, in: A.J. McEvoy (Ed.), Fourth Eur. Solid Oxide Fuel Cell Forum, Lucerne/Switzerland, (2000), pp. 773–782.
[4] C. Kleinlogel, L.J. Gauckler, Sintering and properties of nanosized ceria solid solutions, Soliod State Ionics 135 (2000) 567–573.
[5] P.L. Chen, I.-W. Chen, Reactive cerium (IV) oxide powders by the homogeneous precipitation method, J. Am. Ceram. Soc. 76 (1993) 1577–1583.
[6] S. Wang, H. Inaba, H. Tagawa, T. Hashimoto, Nonstoichiometry of $Ce_{0.8}Gd_{0.2}O_{1.9-x}$, J. Electrochem. Soc. 144 (1997) 4076–4080.
[7] D. Schneither, M. Godickemeier, L.J. Gauckler, Nostoichiometry and defect chemistry of ceria solid solutions, J. Electroceram. 1 (2) (1997) 165–172.
[8] M. Hrovat, A. Bencan, J. Holc, T. Rojac, M. Kosec, Subsolidus phase equilibria in the RuO_2–Bi_2O_3–CeO_2 system, J. Mater. Res. 18 (2003) 1297–1300.
[9] K. Keizer, M.J. Verkerk, A.J. Burggraaf, Preparation and properties of new oxygen ion conductors for use at low temperatures, Ceram. Int. 5 (1979) 143–147.
[10] K. Keizer, A.J. Burggraaf, The effect of Bi_2O_3 on the electrical and mechanical properties of ZrO_2–Y_2O_3 ceramics, J. Mater. Sci. 17 (1982) 1095–1102.
[11] R.D. Shannon, Revised effective ionic radii in halides and chalcogenides, Acta Cryst. A32 (1976) 751–767.
[12] Y. Zhou, M.N. Rahaman, Effect of redox reaction on the sintering of cerium dioxide, Acta Mater. 45 (1997) 3635–3639.
[13] T. Zhang, J. Ma, L.B. Kong, P. Hing, J.A. Kilner, Iron oxide as an effective aid and grain boundary scavenger for ceria-based electrolytes, Solid State Ionics 167 (2004) 203–207.