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ScienceDirect
Ceramics International 38S (2012) S497–S500
CERAMICS INTERNATIONAL
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Cobalt oxide co-doping effect on the sinterability and electrical conductivity of nano-crystalline Gd-doped ceria

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Available online 25 May 2011

Abstract

Nano-crystalline 3 mol% CoO-doped GDC ($Ce_{0.9}Gd_{0.1}O_{1.95}$) powders of high sinterability at lower sintering temperature have been synthesized by deposition–precipitation method. The physical and chemical properties of the obtained powders were characterized by XRD, XPS, BET, EDS and TEM. From sintering studies, CoO-doped GDC can be fully densified (97% relative density) at a lower temperature of 850 °C. It has also been found that the sintered samples have a higher ionic conductivity of 2.38×10^{-2} S cm^{-1} at 600 °C in air.

Keywords: A. Powders: chemical preparation; C. Electrical conductivity; D. CeO_2; E. Fuel cells

1. Introduction

Ceria-based materials have been extensively studied as electrolyte material alternative to yttria-stabilized zirconia for intermediate temperature solid oxide fuel cells (IT-SOFCs) due to their superior ionic conductivity [1]. Among various kinds of doped ceria, gadolinium doped ceria (GDC, $Ce_{0.9}Gd_{0.1}O_{1.95}$) is considered as the most promising electrolyte for IT-SOFCs [2]. However, ceria-based materials generally require high sintering temperature of 1400–1600 °C for densification [3]. A decrease in the sintering temperature can be achieved by decreasing the particle size of the powder to nano-scale, thus increasing the driving force for sintering [4] and/or by addition of sintering aids to increase the sintering rates [5,6].

Yoshida et al. [7] reported that sintering of samaria-doped ceria was significantly promoted by the addition of gallia. Kleinlogel and Gauckler [5,8] reported that the addition of Co_3O_4 strongly enhanced the densification without changing the electrochemical performance of $Ce_{0.8}Gd_{0.2}O_{2-x}$. Zhang et al. [6,9] reported that the addition of Fe_2O_3 or CoO strongly enhanced the densification rate and promoted the grain boundary mobility, thus a lower sintering temperature of ceria was achieved.

The optimum CoO additive concentration has been reported between 1 and 5 mol% for GDC, enabling sintering temperatures between 875 and 1000 °C [10]. Jud et al. [11] estimated the maximum solubility of cobalt in GDC to be less than 0.5 mol% at 900 °C. Results of different authors showed that the conductivity of doped-ceria remains unchanged for CoO concentrations up to 3 mol%, while a significant drop in conductivity was found at >5 mol% [5,8].

It should be noted that these studies on the sintering additives were done where the starting powders have been either commercial powders or doped powders prepared by powder-mixing. In this study, 3 mol% CoO-doped GDC powder has been obtained by deposition–precipitation method and its sinterability and electrical conductivity has been examined.

2. Experimental

The GDC nano-powder (S_{BET} = 68 m^2/g) used in the deposition–precipitation method has been prepared by co-precipitation method and the details of the synthesis procedure was explained elsewhere [12]. In deposition–precipitation method, Na_2CO_3 was used as precipitating agent and added to the solution containing GDC nano-powder and cobalt acetate tetra-hydrate (Aldrich chemicals). The pH of the resulting mixture was kept at 10 under vigorous stirring at 80 °C for 1 h and then aged for 3 h. The obtained precipitate was filtered by a

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0272-8842/$36.00
doi:10.1016/j.ceramint.2011.05.062

centrifuge and washed with hot water. The obtained precipitate was dried at 80 °C for 24 h and calcined at 450 °C for 2 h to obtain 3 mol% CoO-doped GDC powder.

The phase and crystallinity of the samples were identified by X-ray diffractometer (PW 3830). The crystallite size was calculated with Scherer's equation. The morphology and size was obtained by scanning electron microscope (XL-30 FEG ESEM) and transmission electron microscope (TEM, Technai G2F20). The specific surface area was measured by the Brunauer–Emmett–Teller (BET) method. X-ray photoelectron spectroscopy (XPS) was performed in ultra-high vacuum using PHI 5800 instrument.

For observing the sintering behavior, uni-axially formed pellets were pressed at 200 MPa by using cold isostatic pressing (CIP). Shrinkage of the pellets was measured with a dilatometer (Netsch Dil 402C/3/G) up to 1500 °C in air with a heating rate of 3 °C/min. The relative density was estimated by Archimedes method. The electrical conductivity was measured in the temperature range 600–800 °C in air with four-point DC method.

3. Results and discussion

Fig. 1 shows the XRD patterns of CoO-doped GDC powder calcined at 450 °C/2 h. It can be seen from the figure that there were no clear impurity phases in the sample. Wang et al. [13] has also observed no impurity phases for cobalt doped SDC (5 at.% Co) that has been sintered at 1100 °C. Table 1 shows the powder characteristics of CoO-doped GDC. The primary particle size obtained by XRD, BET and TEM analysis was around 8–11 nm.

Fig. 2(a) depicts the overall XPS spectrum of CoO-doped GDC powder calcined at 450 °C/2 h. With the XPS analysis, only core level spectra with highest photo ionization cross section were recorded. In the case of ceria, Ce3d has a higher photo ionization cross section than Ce4d. So, only the Ce3d peaks were rerecorded for obtaining more reliable information. Insert in Fig. 2(a) shows the peaks of Ce3d marked with vertical line and the corresponding binding energies are also shown in the figure. In the case of ceria based materials, the interpretation of Ce3d photoemission spectra is not straight-forward mainly due to the presence of more than 10 peaks and due to multi-electric processes both in Ce^{+4} and in Ce^{+3} states. This leads to

Table 1
Powder characteristics of CoO-doped GDC powder after calcination at 450 °C/2 h.

Surface area	Particle size
BET (m^2/g)	80.2
D_{BET} (nm)	10.4
D_{XRD} (nm)	11.1
D_{TEM} (nm)	8–10

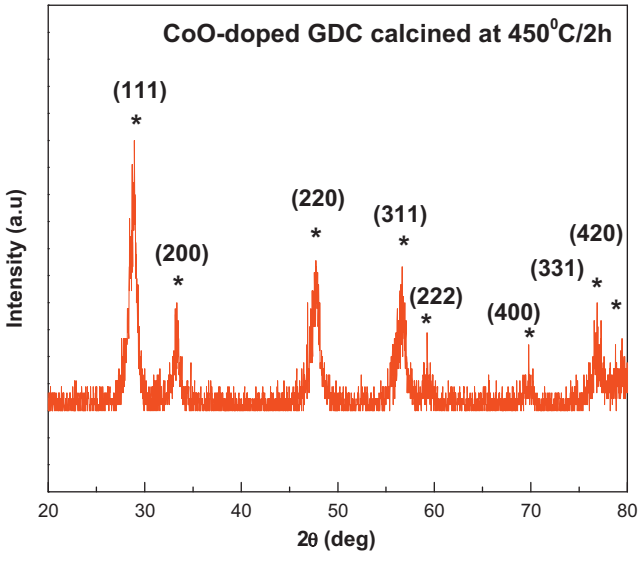
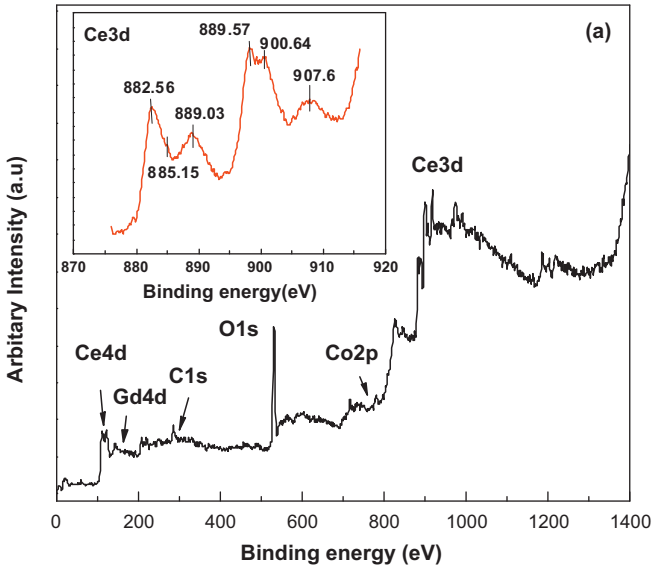


Fig. 1. X-ray diffraction profile of CoO-doped GDC powder prepared by deposition–precipitation method and calcined at 450 °C/2 h.



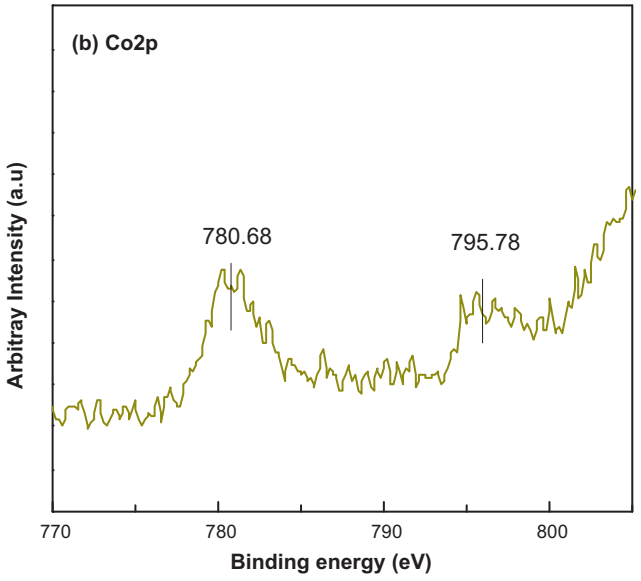


Fig. 2. XPS spectrum of CoO-doped GDC calcined at 450 °C/2 h (a) overall and Ce3d spectrum (b) Co2p spectrum.

extremely complicated spectrum with overlapping peaks if both oxidation states are present. However, it can be seen that most of the peaks are from Ce^{+4} states. Fig. 2(b) shows the core level peaks of Co and the corresponding binding energies are marked in the figure. Two clear peaks can be identified for Co2p. $Co2p_{3/2}$ and $Co2p_{1/2}$ peaks are located at 780.6 and 795.8 eV, respectively [14]. These peaks indicate that the Cobalt is present in oxide state.

Fig. 3 shows the linear shrinkage spectra and the shrinkage rate spectra of CoO-doped GDC green compact. The linear shrinkage starts at a lower temperature of 500 °C and showed a single shrinkage rate maxima at around 820 °C where the densification rate becomes the highest. Appearance of only one maxima of shrinkage rate indicates that the homogeneity of CoO-doped GDC powder compact is mainly due to good powder characteristics with uniform size and distribution. A linear shrinkage of 25% is observed at around 900 °C which indicates that the full densification can be done below 900 °C.

From literature [15], it can be observed that the *in-situ* CoO-doped GDC prepared by flame spray synthesis exhibited a maximum shrinkage rate at 880 °C whereas for conventionally prepared CoO-doped GDC by nitrate-route method it has been observed at 914 °C. In the present study, the temperature of maximum shrinkage rate has been observed at a lower temperature of 820 °C. Based on the comparisons of these different doping methods, it can be concluded that the homogeneity of the dopant phase has an important effect on the sintering properties which can be achieved by different synthesis methods. Hence, by using deposition–precipitation method, the sinterability of GDC has been significantly enhanced by improving the dispersion of the dopant.

Table 2 shows the sintering density as a function of temperature for a holding time of 2 h. As shown in Table 2, sintering at 800 °C achieved a relative density of about 58%. With the increase of sintering temperature to 850 °C, relative density has been drastically increased to 97% which indicates

Table 2
Relative density of CoO-doped GDC at different sintering temperatures for 2 h.

$T_{sintering}$	$\rho_{sintering}$ (%)
800 °C	58
850 °C	97
900 °C	97.5

that the completion of sintering within a short range of temperature (850 °C) can be reached by CoO-doped GDC. This decrease in sintering temperature is believed to be due to a more homogenous dopant distribution of CoO-doped GDC nano-powders obtained by deposition–precipitation method.

Electrical conductivity of CoO-doped GDC samples sintered at 850 °C for 2 h as a function of the temperature is shown in Fig. 4. The ionic conductivity increased with the increase in temperature with activation energy of 0.63 eV. The CoO-doped GDC sample exhibited a conductivity of 2.38×10^{-2} S cm^{-1}at 600 °C. It can be observed from Fig. 4 that the CoO-doped GDC showed a higher conductivity than the un-doped sample. The electrical conductivity of Co-GDC as a function of oxygen partial pressure has been shown in insert of Fig. 4. From the figure it can be observed that the total conductivity is predominantly ionic and remains constant at moderate P_{O_2}. Whereas at low P_{O_2}, the total electrical conductivity increased as P_{O_2} decreased with a rate of $P_{O_2}^{-1/4}$ that indicated the appearance of electronic conduction. The improvement in the ionic conductivity of CoO-doped GDC can be possible due to (i) a reduction in the lattice strain of GDC by Co and (ii) the formation of Co-rich grain boundary layer [13]. Further studies on the reasons for the improvement in the ionic conductivity of CoO-doped GDC than compared to undoped GDC would be the topic of the forthcoming paper.

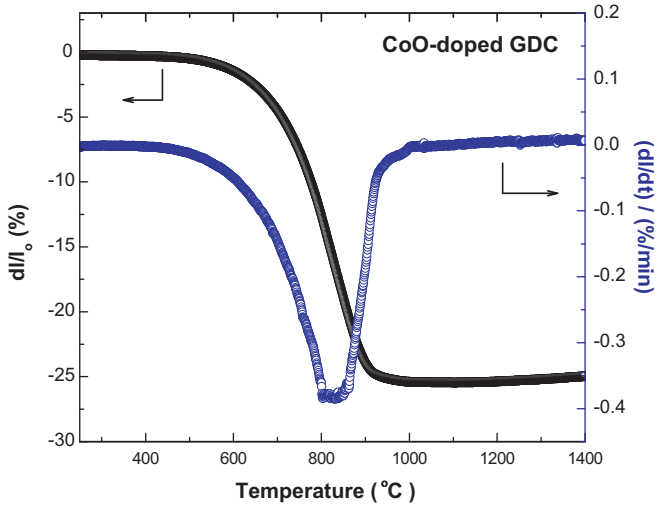


Fig. 3. Linear shrinkage and shrinkage rate of CoO-doped GDC pellet.

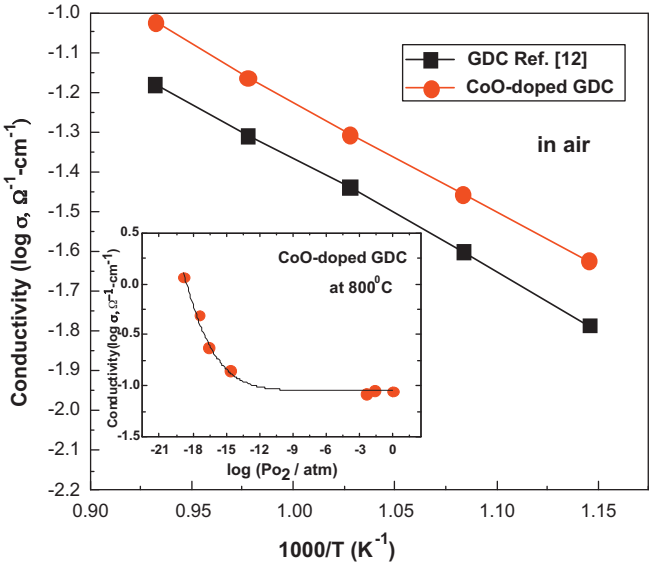


Fig. 4. Temperature and oxygen partial pressure dependence of the electrical conductivity at 800 °C of CoO-doped GDC prepared by deposition–precipitation method. The data is fitted with $\sigma = \sigma_{ion} + \sigma_0 \times P_{O_2}^{-1/4}$.

4. Conclusions

Nano-crystalline 3 mol% CoO-doped GDC powder has been synthesized by deposition–precipitation method. The calculated crystallite size obtained from XRD, BET and TEM were around 8–11 nm. A relative density of 97% is achieved at comparatively lower sintering temperature of 850 °C. Additionally, CoO-doped GDC showed a fairly high ionic conductivity of 2.38×10^{-2} S cm^{-1} at 600 °C in air which further demonstrates the use of this material as electrolyte for IT-SOFCs.

Acknowledgments

This work was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

References

[1] B.C.H. Steele, Material science and engineering: the enabling technology for the commercialization of fuel cell systems, Journal of Materials Science 36 (5) (2001) 1053–1068.

[2] B.C.H. Steele, Appraisal of $Ce_{1-y}Gd_yO_{2-y/2}$ electrolytes for IT-SOFC operation at 500 °C, Solid State Ionics 129 (2000) 95–110.

[3] P. Duran, C. Moure, J.R. Jurado, Sintering and microstructural development of ceria-gadolinia dispersed powders, Journal of Materials Science 29 (1994) 1940–1948.

[4] P.L. Chen, I.W. Chen, Sintering of fine oxide powders: I, Microstructural evolution, Journal of the American Ceramic Society 79 (12) (1996) 3129–3141.

[5] C. Kleinlogel, L.J. Gauckler, Sintering and properties of nanosized ceria solid solutions, Solid State Ionics 135 (2000) 567–573.

[6] T. Zhang, P. Hing, H.T. Huang, J. Kilner, Sintering and grain growth of CoO-doped CeO_2 ceramics, Journal of the European Ceramic Society 22 (2002) 27–34.

[7] H. Yoshida, K. Miure, J. Fujita, T. Inagaki, Effect of gallia addition on the sintering behavior of samaria-doped ceria, Journal of the American Ceramic Society 82 (1) (1999) 219–221.

[8] C.M. Kleinlogal, L.J. Gauckler, Mixed electronic-ionic conductivity of cobalt doped cerium gadolinium oxide, Journal of Electroceramics 5 (3) (2000) 231–243.

[9] T. Zhang, P. Hing, H. Huang, J. Kilner, Densification, microstructure and grain growth in the CeO_2–Fe_2O_3 system ($0 \leq$ Fe/Ce $\leq 20\%$), Journal of the European Ceramic Society 21 (2001) 2221–2228.

[10] C.M Kleinlogel, L.J. Gauckler, Sintering of nanocrystalline CeO_2 ceramics, Advanced Materials 13 (2001) 1081–1085.

[11] E. Jud, Z. Zhang, W. Sigle, L.J. Gauckler, Microstructure of cobalt doped ceria solid solutions, Journal of Electroceramics 16 (2006) 191–197.

[12] D. Hari Prasad, H.-R. Kim, J.-S. Park, J.-W. Son, B.-K. Kim, H.-W. Lee, J.-H. Lee, Superior sinterability of nano-crystalline gadolinium doped ceria powders synthesized by co-precipitation method, Journal of Alloys and Compounds 495 (2010) 238–241.

[13] Z. Wang, S.-I. Hashimoto, M. Mori, Investigation and optimization of interface reactivity between $Ce_{0.9}Gd_{0.1}O_{1.95}$ and $Zr_{0.89}Sc_{0.1}Ce_{0.01}O_{2-\delta}$ for high performance intermediate temperature-solid oxide fuel cells, Journal of Power Sources 193 (1) (2009) 49–54.

[14] J. Liu, Z. Zhao, J. Wang, C. Xu, A. Duan, G. Jiang, Q. Yang, The highly active catalysts of nanometric CeO_2-supported oxides for soot combustion, Applied Catalysis B, Environmental 84 (2008) 185–195.

[15] E. Jud, L. Gauckler, S. Halim, W. Stark, Sintering behavior of in situ cobalt oxide-doped cerium-gadolinium oxide prepared by flame spray pyrolysis, Journal of the American Ceramic Society 85 (9) (2006) 2970–2973.