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Effect of Bi_2O_3 addition on the sintering and microstructural development of gadolinia-doped ceria ceramics

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Abstract

The effect of small amounts (0.2–2.0 wt.%) of bismuth oxide on the sintering behavior and microstructural development of $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) submicronized powders has been studied using XRD for the lattice parameter measurements, the constant heating rate (CHR) method in air to monitor the shrinkage kinetics of powder compacts, and scanning electron microscopy (SEM) to study the microstructure of the sintered samples. Sintering of GDC compacts was significantly improved by adding small amounts of Bi_2O_3 ($\leq$2.0 wt.%), and samples of doped-GDC sintered at 1200–1400 °C for 2–4 h were dense bodies (98–99.5% of theoretical density). Measurements showed that the addition of Bi_2O_3 could reduce the sintering temperature by about 250–300 °C lower than that for undoped-GDC samples. A liquid phase-assisting mechanism was assumed as the main cause for the enhancement of the densification process. The average grain size of doped-GDC sintered samples grew with the increasing of Bi_2O_3 addition up to 1.0 wt.%, and then decreased indicating a poor wetting properties of the formed liquid phase.

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Keywords: Sintering; Grain growth; Microstructure-final; Electrical conductivity; Bi_2O_3 doped ceria

1. Introduction

Although YSZ (yttria stabilized zirconia with 8 mol% Y_2O_3) represents the state of the art electrolyte for high temperature (800–1000 °C) solid oxide fuel cells (SOFCs),[1] but many problems related to the correct use of the other components (anode, cathode, and interconnector) of the SOFC are to be present during service at the above operating conditions. Therefore, a lower operating temperature becomes necessary to overcome several difficulties. Being the electrolyte the most important component of the SOFC, many efforts are addressed to the search of new ionic conductor ceramics having a high ionic conductivity within the 500–700 °C temperature range. Ceria-based materials are chosen as the best electrolyte candidate for these operating conditions. They have an ionic conductivity much higher that YSZ at intermediate temperature, but these ceramics requires sintering temperatures in the range of 1300–1600 °C to full density[2–5] leading, thus, to microstructures with a grain size too large and, therefore, with very poor mechanical properties. Although many attempts to lower the sintering temperature of the ceria-based ceramics have been carried out in the last decade, the use of transition metal oxide seems to be the most effective additive in reducing this. However they introduce some electronic conduction, which can detrimentally affect the oxide-ion conductivity.[6–9] Recently Zhang et al.[10–12] proposed the use of Fe_2O_3 as a good sintering promoter for ceria-based ceramics, and Yoshida et al.[13] and more recently Lee et al.[14] studied the effect of galia additions on the sintering behavior of samaria doped- and gadolinia-doped-ceria, respectively. It is surprising to note that there are not any reports in the literature concerning the densification of commercial gadolinia-doped ceria powders by using Bi_2O_3 as a sintering promoter.

The aim of the present paper is to study the effect of different doping levels of Bi_2O_3, at our best knowledge for the first time, on the sintering behavior and microstructural development of gadolinia-doped ceria (GDC) submicronized powders, leading to establish the minimal doping level required to optimize both sintering and microstructure of the Bi_2O_3-doped GDC ceramics.

2. Experimental procedure

Commercial gadolinia-doped ceria $Ce_{0.9}Gd_{0.1}O_{1.95}$ powders (Rhodia GmbH, FRG) with an average particle size of 0.38 μm and specific surface of 12.4 m^2/g, was used as starting raw material, which is referred to as GDC powder thereafter. The dopant,

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in the form of bismuth nitrate dissolved in ethanol, was added to a GDC/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 green density of the powder compacts was in the order of 50% theoretical density. Sintering was performed in air at a constant heating rate (CHR) of 2 °C/min up to 1600 °C in a Netzsch dilatometer (model 407/E of Geratebau, Selb.Bayern, Germany). The samples were also isothermally sintered in air at 1400 °C, which was held for times from 0 to 8 h.

The density of the sintered samples was measured by the Archimedes method in water. In order to study the possible influence of the Bi_2O_3 additive on the crystalline structure of the prepared samples these were, after calcining, heat-treated at 1200–1400 °C for 2 h, milled in an agate mortar, and then characterized by X-ray diffraction (XRD) with a Siemens diffractometer (model D-5000, Erlangen, Germany) using nickel-filtered Cu Kα radiation ($\lambda = 0.15405$ nm). An internal standard was used for the lattice parameter measurements. Besides this, a powder mixture containing GDC and Bi_2O_3 50/50 in wt.% was homogenized and heat-treated for several hours at 850–1200 °C for 2 h. The new formed phases, if any, were also investigated by XRD.

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 intercept method on the surface of polished and thermally etched sintered samples. The size of at least 300 grains was taken into account.

3. Results and discussions

3.1. X-ray diffraction study

The XRD study carried out on the doped-GDC samples sintered in the temperature range of 1200–1400 °C, as it is shown in Fig. 1, did not show the presence of free Bi_2O_3 or secondary peak phases, i.e. if some new phases were formed, the amounts was too small to be detected by X-ray diffraction.

However the XRD peaks for doped-GDC samples were slightly shifted to smaller angles with increasing Bi_2O_3 content up to about 1.0 wt.%, but with Bi_2O_3 additions above that concentration the peaks were not shifted further. The shift to smaller angles indicates that the lattice constant is increased when Bi_2O_3 is added to the GDC samples. Such an increase in the lattice constants can be considered as to be due to the substi-

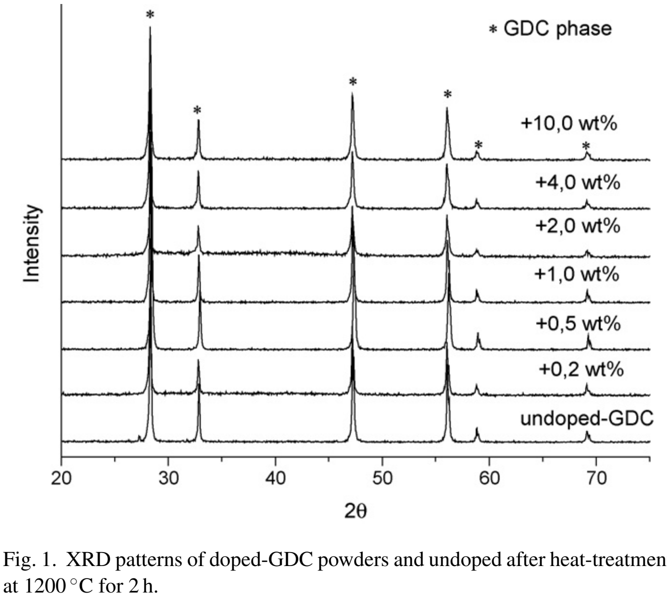

Fig. 1. XRD patterns of doped-GDC powders and undoped after heat-treatment at 1200 °C for 2 h.

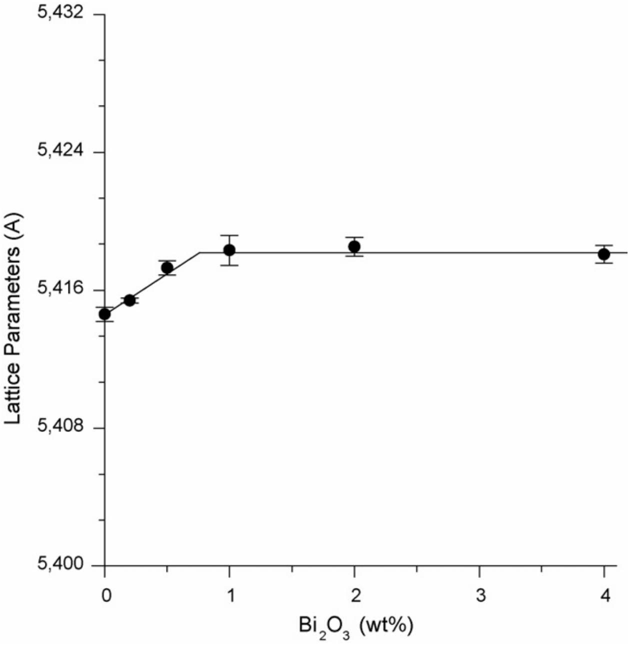

Fig. 2. Lattice parameter of the GDC-Bi_2O_3 composites (1400 °C–2 h) as a function of the Bi_2O_3 content.

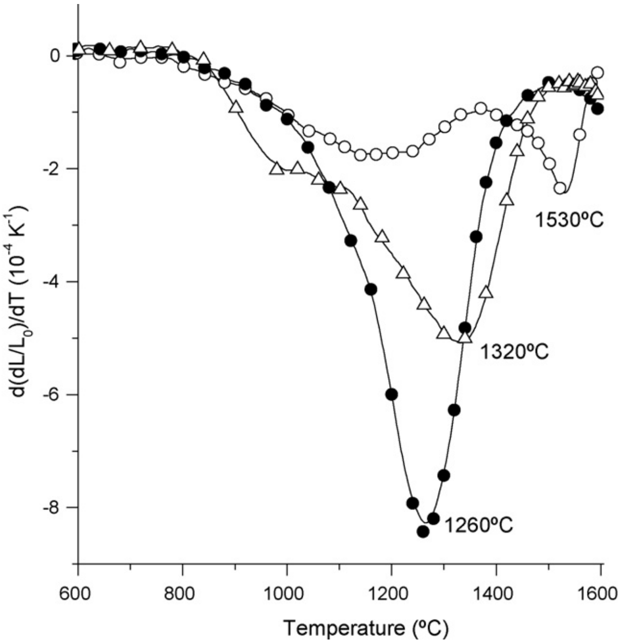

Fig. 3. Effect of sintering temperature on shrinkage rate for: (○) undoped-GDC, (△) +0.5 wt.% Bi_2O_3 and (●) +2.0 wt.% Bi_2O_3.

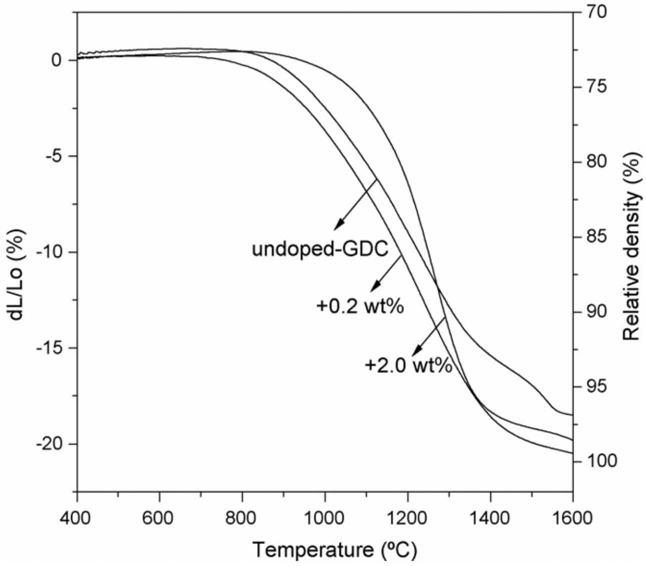

Fig. 4. Effect of sintering temperature on linear shrinkage.

tution of larger Bi^{3+} ions (0.117 nm) for the smaller Ce^{4+} ions (0.097 nm) in the GDC structure. Such substitution reaction can be described, taking into account the Kröger-Vink notation, by the following equation:

$$Bi_2O_3 \xrightarrow{CeO_2} 2Bi'_{ce} + V''_O + 3O^x_O$$

From that equation the formation of oxygen vacancies because of charge compensation should be assumed.

Therefore, from the above results we can estimate that Bi_2O_3 dissolves in the GDC structure, as shown in Fig. 2, for about 0.8 wt.% Bi_2O_3 addition.

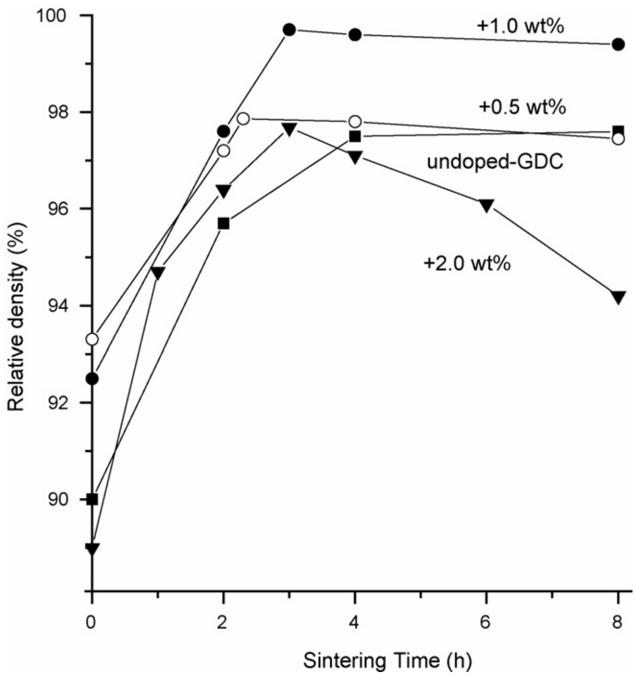

Fig. 5. Effect of sintering time on the relative density of the samples sintered at 1400 °C.

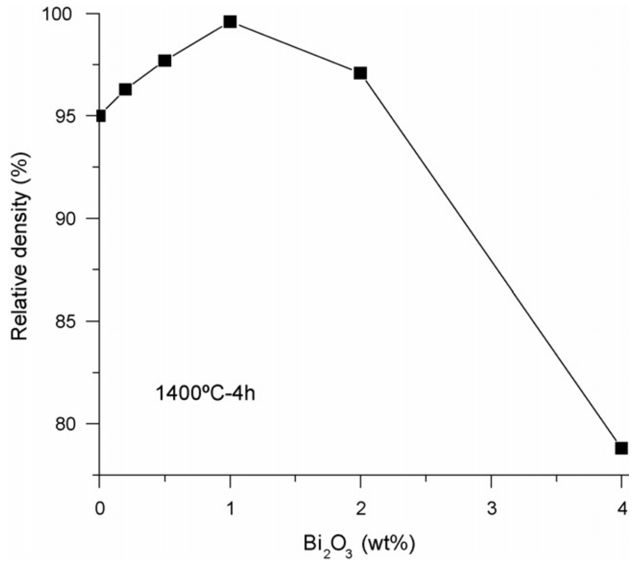

Fig. 6. Sintered density as a function of Bi_2O_3 content.

3.2. Non-isothermal sintering

The sintering behavior of GDC powders doped with different amounts of Bi_2O_3 is shown in Figs. 3 and 4. The shrinkage rate spectra $d(dL/L_0)/dT$ (Fig. 3) and the relative density (Fig. 4) are plotted as a function of temperature for different bismuth oxide concentration. The curve for 1.0 wt.% Bi_2O_3-doped GDC sample in Fig. 3 exhibits a similar shrinkage trend to that of 0.5 wt.% Bi_2O_3-doped GDC and, for clarity, it has been omitted. As it can be seen, the Bi_2O_3 doping is quite effective in enhancing the densification of GDC when its content was $\geq$0.5 wt.%, and it is clear from that figure that the maximum shrinkage rate strongly

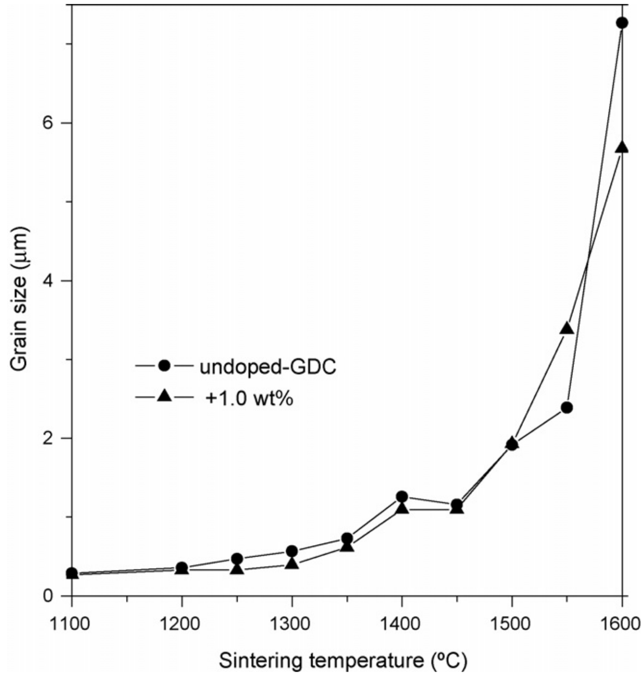

Fig. 7. Grain size as a function of sintering temperature for undoped-GDC and 1.0 wt.% Bi_2O_3-doped GDC samples.

increases with increasing Bi_2O_3 content and, for example, a doping of GDC sample with 2.0 wt.%, this was a factor of 2–5 higher compared to undoped-GDC ones. From Fig. 4, it can be observed that the undoped-GDC samples do not reached its final shrinkage below 1600 °C with a shrinkage of about 18%, while the samples containing 0.2 wt.% Bi_2O_3 reached its final shrinkage at about 1450 °C and a shrinkage of 21%. From that figure, it is also clear that the T_s, i.e. the temperature at which the relative density of the sintered sample attains 95% of theoretical density, decrease from about 1580 to 1370 °C, i.e. more than 200 °C with the only addition of 0.2 wt.% Bi_2O_3. It must be mentioned that all samples reached 96–99% of theoretical density at the end of the non-isothermal sintering process at 1600 °C.

3.3. Isothermal sintering

The effect of the Bi_2O_3 additions in enhancing the densification of GDC ceramics was also evidenced by studying the evolution of the density of the samples as a function of the sintering time. As it is shown in Fig. 5, the density of the undoped-GDC samples monotonically increase with increasing sintering time, reaching a density of 97.6% after sintering

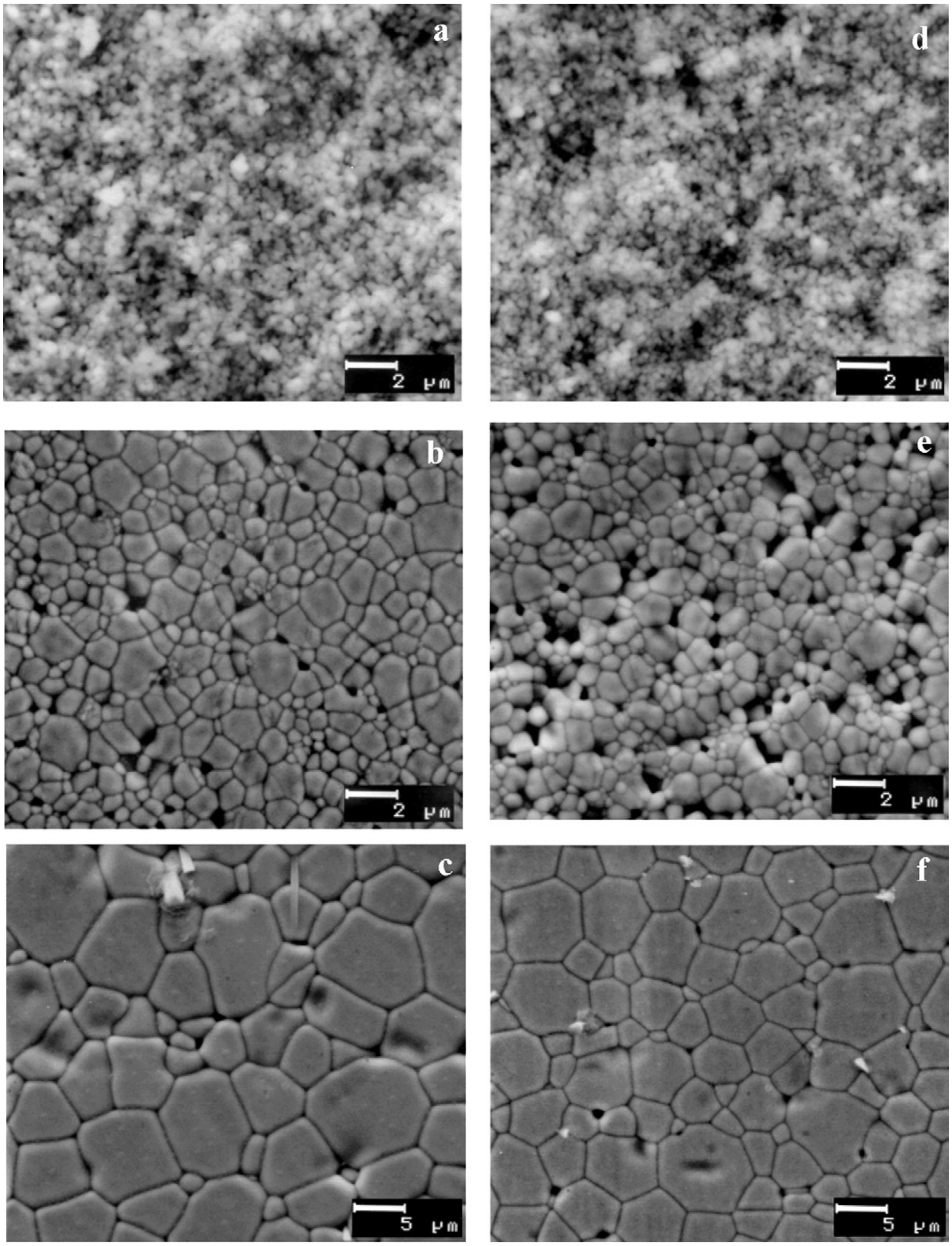

Fig. 8. SEM micrographs of samples sintered at 1200, 1450 and 1600 °C for 2 h of (a), (b), (c) undoped and (d), (e) and (f) 1.0 wt.% Bi_2O_3-doped GDC samples, respectively.

at 1400 °C for 8 h. However, the doped-GDC samples attain a density as high as 97.9 and 99.7% of theoretical density after sintering time of about 2 and 3 h for the samples containing 0.5 and 1.0 wt.% Bi_2O_3, respectively. As it can be seen, for higher sintering time the density of the doped-GDC samples slightly decreased, which indicates that although the addition of small amounts of Bi_2O_3 to GDC powders strongly enhances the sintering behavior of these ceramics, but its density decreased when the sintering temperatures are relatively high (≥1350–1400 °C), and/or the sintering time is too long (≥2–3 h). This fact is particularly clear when the Bi_2O_3 content is 2.0 wt.%. Fig. 6 shows the sintered density of GDC samples as a function of Bi_2O_3 content and, it is shown that the sintered density increases with increasing Bi_2O_3 up to 1.0 wt.%. For higher Bi_2O_3 concentration, the sintered density rapidly deteriorated as shown in such a figure, i.e. a dedensification phenomenon is present[15] which can be attributed, in principle, to both the evaporation of Bi_2O_3 and the release of oxygen gas from some reduction of CeO_2 to Ce_2O_3, according to the following equation:

$$2CeO_2 \rightarrow Ce_2O_3 + \frac{1}{2}O_2$$

From all the above, it could be assumed that an optimal amount of Bi_2O_3 to be used as an aid for sintering of GDC ceramics is 1.0 wt.%. In the same way, an optimized sintering temperature could be located in the 1350–1400 °C range, which can be considered as a competitive temperature for a co-sintering process.

3.4. Microstructural development

Taking into account the above results, a study of the evolution of the grain size as a function of the temperature was carried out only on the doped-GDC samples containing 1.0 wt.% Bi_2O_3, as shown in Fig. 7. For comparison, the evolution of the grain size in the undoped-GDC samples is also shown. As it can be seen, there is a first region up to 1200 °C, the sample was only 87% dense and with open porosity, in which the grain size is hardly affected by the presence of the additive. It can be associated with the early stage-sintering[16] and, on the other hand, the wetting properties of the formed liquid phase are, probably, very poor at that temperature impeding, thus, the diffusion of some material. A second region, above 1200 °C and up to 1400 °C in which a little grain growth but with a homogeneous grain size took place.[17,18] At this temperature range, the viscosity of the liquid phase will be much lower than that at 1200 °C, and the grain size monotonically increases with increasing temperature. This evolution of the grain size could be related with the intermediate-stage sintering, i.e. in which the samples are ≥95% dense and closed porosity. In the undoped-GDC samples the grain size increases with increasing temperature up to 1400 °C, according to a sintering process dominated by a solid-state diffusion mechanism.[19] Above 1400 °C, i.e. at the last-stage sintering, the grain growth in both kinds of samples was much faster than in the second region and, according to the suggestions of Kingery et al.,[20] a rapid grain growth by a solid-state reaction mechanism took place. Fig. 8 shows the SEM micrographs corresponding to these samples sintered at different temperatures.

4. Conclusions

From the above experimental described results, we can state the following: (a) additions of 0.2–2.0 wt.% Bi_2O_3 onto GDC submicronized powders all of them promoted densification of this ceramic electrolyte achieving almost theoretically dense bodies (≥99.8%), when GDC samples containing 1.0 wt.% Bi_2O_3 were sintered at 1400 °C for 4 h, i.e. almost 200 °C lower than for undoped-GDC samples, (b) the extremely improved densification rate was believed to take place by a liquid phase-assisting mechanism, (c) the solubility limit of Bi_2O_3 in the GDC structure was about 0.8 wt.% in the temperature range of 1200–1400 °C, and (d) Bi_2O_3 additions retarded or at least do not promotes grain growth in doped-GDC samples sintered up to or below 1350–1400 °C, which was assumed to be due to a poor wetting properties of the formed liquid phase.

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References

1. Minh, N. Q., *J. Am. Ceram. Soc.*, 1993, **76**, 563.
2. Kleinlogel, C. and Gauckler, C. J., *Solid State Ionics*, 2000, **135**, 567.
3. Zhou, Y. C. and Rahaman, M. N., *J. Am. Ceram. Soc.*, 1995, **78**, 981.
4. Van Herle, J., Horita, T., Kawada, T., Sakai, N., Yokokawa, M. and Dokiya, M., *Solid State Ionics*, 1996, **86/88**, 1255.
5. Duran, P., Moure, C. and Jurado, J. R., *J. Mater. Sci.*, 1994, **29**, 1940.
6. Fagg, D. P., Kharton, V. V. and Frade, J. R., *J. Electroceram.*, 2002, **9**, 199.
7. Tuller, H. L., *Solid State Ionics*, 2000, **131**, 143.
8. Chiang, Y. M., Lavik, E. B., Kosacki, I., Tuller, H. L. and Ying, J. Y., *J. Electroceram.*, 1997, **1**, 7.
9. Steele, B. C. H., Hori, K. M. and Uchino, S., *Solid State Ionics*, 2000, **135**, 445.
10. Zhang, T. S., Hing, P., Huang, H. T. and Kilner, J. A., *J. Eur. Ceram. Soc.*, 2001, **21**, 2221.
11. Zhang, T. S., Hing, P., Huang, H. T. and Kilner, J. A., *Solid State Ionics*, 2002, **148**, 567.
12. Zhang, T. S., Ma, J., Kong, L. B., Chan, S. H., Hing, P. and Kilner, J. A., *Solid State Ionics*, 2004, **167**, 203.
13. Yoshida, H., Miura, K., Fujita, J. and Inagaki, T., *J. Am. Ceram. Soc.*, 1999, **82**, 219.
14. Lee, J. S., Choi, K. H., Ryu, B.-K., Shin, B. C. and Kim, I. S., *Mater. Res. Bull.*, 2004, **39**, 2025.
15. Balzer, B., Hagemeister, M., Kocher, P. and Gauckler, L. J., *J. Am. Ceram. Soc.*, 2004, **87**, 1932.
16. German, R. M., *Liquid Phase Sintering*. Plenum Press, New York, USA, 1985.
17. Cameron, C. P. and Raj, R., *J. Am. Ceram. Soc.*, 1988, **71**, 1031.
18. Nadaud, N., Kim, D. and Boch, P., *J. Am. Ceram. Soc.*, 1997, **80**, 1208.
19. Chen, P. L. and Chen, I.-W., *J. Am. Ceram. Soc.*, 1996, **79**, 1793.
20. Kingery, W. D., Bowen, H. K. and Uhlmann, D. R., *Introduction to Ceramics* (*2nd ed.*). Wiley, New York, 1976.