A Comparative Study of Conventional and Microwave Sintering of $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$ Ceramic

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Abstract The nanoparticles of $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$ (BCGO) with $x = 0.01$ and 0.02 mol% Gd^{3+} respectively, were synthesized by the polymeric precursor method. The nanocrystals analyzed by X-ray diffraction (XRD) displayed an orthorhombic perovskite-type structure. The sintered samples were characterized using Archimedes method, field emission scanning electronic microscopy (FE-SEM), and dilatometric measurements are reported. The values obtained relative to the average crystallite sizes calculated by the Scherrer equation were found to be dependent on Gd dopant concentration in the samples under investigation. The samples were sintered via both conventional and microwave sintering methods at 1480°C for 4 h and at 1370°C for 1 h respectively. By applying a heating rate of $50^\circ\text{C min}^{-1}$ in a microwave oven, a satisfactory final density (95.1% of the theoretical density) was obtained using relatively lower temperatures compared to the conventional method. Both sintering methods were successfully employed towards obtaining dense BCGO ceramic. Comparatively, however, domestic microwave sintering was found to bear advantages

over conventional sintering. Among such advantages include rapid heating, selective material coupling in addition to the enhancement of reaction kinetics. These relevant merits, in essence, render microwave sintering suitably more attractive for the synthesis of diverse ceramic materials.

Keywords Proton conductors · Gadolinium · Barium cerate · Microwave sintering

1 Introduction

The nonstoichiometric barium cerate $\text{BaCeO}_{3-\delta}$ (BCO) have been extensively studied due to its potential applications in solid oxide fuel cells (SOFC) [1–3], hydrogen separation membranes, gas sensors [4, 5], electrocatalysis technology [6] and heterogeneous photocatalytic activities [7]. However, barium cerate has been broadly studied as proton-conducting electrolytes for SOFC because of their favorable properties such as high conductivity [8–10].

The increasing demand for clean, secure, and sustainable energy sources has stimulated great scientific and industrial interest in development of fuel cells. Fuel cells are devices that directly convert chemical fuel to electricity. An intense effort has been done for the development of the solid oxide fuel cells (SOFCs) represent the cleanest, most efficient, and versatile energy conversion system [11, 12].

In this context, the effects of the addition of dopants such as Gd^{3+} ions on proton conductivity are of prime importance because allow to increase the concentration of proton in BaCeO_3 . Thus, the gadolinium-doped barium cerate $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$ ceramic materials, known as (BCGO) is a proton-conducting solid electrolyte with a high conductivity in intermediate-temperature in SOFCs applications [13–17]. Proton conductors have attracted

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considerable attention as a result of their low activation energy and high ionic conductivity at relatively low temperatures [18]. In the development process of electrolytes (i.e., solid oxide fuel cells with ion-permeable electrolytes), high-final densities of the sintered bodies are particularly desirable once they contribute towards improving the efficiency of energy conversion by preventing the permeation of other gases [19, 20]. Proton-conducting perovskite oxides have been proposed in the literature as new candidate electrolyte material for SOFCs. These oxides can achieve high proton-conductivity at fairly low temperatures (350–600 °C) by virtue of their relatively low activation energy when it comes to proton conduction (0.3–0.6 eV) [21].

Reports in the literature show that long processing time and high sintering temperatures are required if one is to obtain dense ceramic materials such as BCO. Nonetheless, it is well-known that the increasing either the sintering temperature or sintering time normally results in a large barium evaporation and subsequent chemical barium deficiency in the final product. This deficiency inevitably leads to a decline in total conductivity [22–25]. However, some works reported in the literature have demonstrated the superiority of microwave sintering compared to other techniques [26–29].

The microwave sintering can give rise to dense materials at lower temperatures and shortened sintering periods compared to those of conventional sintering [30–33]. Isolating materials such as silicon dioxide or alumina are supposed to be heated above 600 °C in order to generate time-dependent electric dipoles that can absorb the microwave energy [34]. In conventional furnaces, heat is transported from the walls to the sample and its temperature increases slowly until equilibrium is reached. The use of microwaves allows an inversion of the heat profile as the material itself is subjected to heat treatment. This contributes towards reducing thermal strain and may give rise to higher relative densities [35].

Several alternatives to conventional sintering of green compacts composed of nanosize particles have been proposed aiming at improving the mechanical and electrical properties associated with higher density and smaller average grain size [36]. In this context, microwave radiations are found to be advantageous as a result of the economy of energy and time during processing [37].

This work seeks to report the findings of our study conducted on (BCGO) pellets sintered by both conventional and microwave methods with the aim of comparing the effect of methodology on the stability and sinterability of as-prepared BCGO ceramics.

2 Experimental

2.1 Synthesis

For the synthesis of BCGO powders ($\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$ and $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$) by the polymeric precursor method, the cerium citrate was prepared by the addition of 1×10^{-2} mol of hexahydrated cerium (III) nitrate $[\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$ in an aqueous solution of citric acid using the metal/acid molar ratio of 1:3. Similarly, barium citrate was obtained by the reaction of $\text{Ba}(\text{NO}_3)_2$ with a citric acid solution using the same metal/acid ratio. The citrates were mixed and kept under constant stirring. Afterwards, gadolinium (III) oxide $[\text{Gd}_2\text{O}_3, 99.9\% \text{ Aldrich}]$, dissolved in a minimum amount of nitric acid, was used as doping agent and added to the first solution. Complete dissolution resulted in a clear yellow solution. Ethylene glycol was then added in the proportion by mass of 60:40 of citric acid and ethylene glycol in order to promote the polyesterification reaction. The polyester was subsequently placed in an oven to be thermally treated at 300 °C for 2 h in air so as to obtain the solid resin. The resins were heat-treated at 950 °C for 2 h in a conventional furnace to obtain the crystalline powder.

2.2 Sintering

BCGO samples were formed into pellets ($\varnothing = 9$ mm, $h = 3$ mm) and isostatically pressed at 210 MPa resulting in green densities close to 52% of the theoretical density. Sintering study was carried out in a dilatometer at temperatures up to 1550 °C. The pellets were sintered at 1480 °C for 4 h in a conventional furnace (the heating and cooling rates were set at $10^\circ\text{C min}^{-1}$) and at 1370 °C for 1 h in a microwave furnace at a heating rate of $50^\circ\text{C min}^{-1}$ followed by cooling (a cooling rate of approximately $10^\circ\text{C min}^{-1}$) in a similar experimental setup as described in the literature [38]. A modified domestic microwave furnace (2.45 GHz, 850 W) containing a SiC susceptor was used in order to absorb the microwave energy. The temperature profile was measured using Pt–13% Rh thermocouples placed 3 mm above the sample surface. The sintered samples were characterized by the Archimedes method. Prior to immersion, the open pores are filled with a fluid, as, for example, the water. For these test, the sample is first weighed dry (W_1), then weighed again after fluid impregnation (W_2), and finally weighed while immersed in water (W_3). In general, a wire is normally used to suspend the sample in water, and its weight is also measured in water. Hence, the density (ρ) of the sintered samples is then calculated from the weight determinations, according to the following Equation [39]:

$$\rho = \frac{w_1 \rho_w}{w_2 - (w_3 - w_w)}$$

where ρw is the density of water.

2.3 Characterization

Structural characterizations of the ceramics were performed by X-ray diffraction (XRD) using a Rigaku-DMax (model 2500 PC) diffractometer with a Cu-K α radiation ($\lambda = 1.54060 \text{ \AA}$) source and graphite monochromator. Measurements were carried out over an angular range of $10^\circ \leq 2\theta \leq 80^\circ$ using scanning steps of 0.02° and a fixed counting time of 6 s. Divergence, scattering, and receiving radiation slit values were 1° , 1° , and 0.3 mm, respectively. Dilatometric study was conducted in a dilatometer (Netzsch 402, Germany) up to the temperature of 1550°C at $10^\circ\text{C min}^{-1}$.

The morphologies and fired density of the final samples were observed by field emission scanning electron microscopy (FE-SEM) using a Carl Zeiss Supra 35-VP model (Germany) microscope operated at 6 kV.

3 Results and Discussion

3.1 X Ray Diffraction

In order to find out the lowest temperature to obtain the pure BCGO phase, we have selected one of the compositions ($\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$) to perform a thermal study by varying the thermal treatments. Figure 1 shows the XRD patterns of BCGO (10 mol% Gd) ceramic powders prepared via the polymeric precursor method calcined at 700, 800, 900 and 950°C for 2 h. As showed, the changes of the phases relative to temperature can be easily monitored by means of the XRD patterns. Higher heat treatment temperatures were

Fig. 1 XRD pattern of BCGO powders relative as function of the temperature

found to improve the purity and crystallinity of the powders. Pure BCGO was produced through thermal treatment at a temperature of 950°C for 2 h. For lower temperatures, we identified some traces of additional peaks corresponding to impurity phases, which are attributed to the BaCO_3 phase and are probably as a result of the existence of barium vacancies in the structure.

Figure 2 shows typical XRD patterns of $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$ and $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ crystals synthesized at 950°C for 2 h by the polymeric precursor method. The sharp and well-defined diffraction peaks indicate a high degree of crystallinity; in other words, all crystals are structurally ordered at long range. Figure 2 illustrates the XRD patterns of the monophasic samples of $\text{BaCe}_{1-x}\text{Gd}_x\text{O}_{3-\delta}$ (crystals with $x = 0.01$ and 0.02) mol% Gd^{3+} . The diffraction peaks can be assigned to the orthorhombic perovskite-type structure and are in line with the Joint Committee for Powder Diffractions Standards Card (JCPDS card No 22-0074). The main peaks correspond to (220), (122), (213), (422), (233) and (440) planes.

The average crystallite sizes for BCGO samples were calculated based on the XRD data and the Scherrer equation, and are shown in Table 1. With the increasing dopant

Fig. 2 XRD pattern of BCGO powders with different concentration of Gd^{3+} ions obtained following thermal treatment at 950°C for 2 h

Table 1 Average crystallite size of BCGO samples

Sample	Average crystallite size (nm)
$\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$	38.18
$\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$	30.48

Fig. 3 Dilatometric curve obtained at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ ($\Delta L/L_0$) and derivative of the linear shrinkage curve ($d(\Delta L/L_0)/dt$) as function of the temperature

concentration, the crystallinity and crystallite size of the BCGO particles decreased.

3.2 Dilatometric Analysis and Sintering

The synthesis method and the conformation of the particles gave rise to areas of agglomerated powder. These nanometric agglomerated powder displayed a stronger tendency for sintering at lower temperatures ($1190\text{ }^{\circ}\text{C}$) compared to non-agglomerated particles by virtue of their relatively higher quantity of contact points, which contribute towards the formation of pores and defects [40]. Oddly enough though, very high heating rates may favor the simultaneous occurrence of both these situations, thereby preventing the occurrence of defects.

Figure 3 depicts the dilatometric profile of the samples sintered using the heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. As can be observed, the dilatometric curves showed two sintering stages at $1190\text{ }^{\circ}\text{C}$ (P1) and $1370\text{ }^{\circ}\text{C}$ (P2). By considering similar studies reported in the literature [40–42], we suggest that the first stage is related to the sintering of agglomerates while the second stage is associated with dispersed particles,

Fig. 4 **a** SEM micrograph of BCGO (20 mol% Gd) after conventional sintering; **b** XRD pattern for BCGO; **c** XRD pattern for CeO_2

attributing them to advanced sintering mechanisms. The unambiguous determination of a sintering mechanism is complicated by the possible effects of combined mechanisms and, in the case of diffusion, by the similarity of the time dependence of surface and volume diffusion [43].

In the first moment, the pellets were conventionally sintered at 1480 °C for 4 h using an open crucible. From the FE-SEM images (Fig. 4a) one can observe the existence of two different compounds in the same sintered ceramic body. XRD patterns clearly index the both formed phase are attributed to the formation of both phases (Fig. 4b–c). Clearly, one phase matches with the fluorite structure of CeO_2 (JCPDS card No 01-075-0162) while the other one matches with the orthorhombic perovskite-type BCGO (JCPDS card No 22-0074). This effect has been reported in the literature by Tong et al. [44]. They demonstrated that given an increase in

sintering temperature or sintering time of $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ ceramics, grain growth and densification are found to be improved albeit this normally results in barium deficiency and the emergence of deleterious second phases such as Y_2O_3 .

In order to obtain highly dense and well sintered bodies, we opted for optimizing the sintering process as shown in the scheme, Fig. 5 a–b. The pellets were placed on a BCGO powder layer (in a closed crucible) for the powder to act as a protective barrier during sintering. By so doing, we were able to prevent the evaporation of the Ba^{2+} ions as such effect is undesirable.

Figure 5c–d shows the FE-SEM images of the sintered samples. From these images, it is possible to compare the effect of the methodology on the microstructure of these materials. We can see that both sintering methods were

Fig. 5 Schematic illustration of BCGO samples sintered by (a) microwave sintering and (b) conventional sintering. FE-SEM images of BCGO samples sintered by (c) microwave sintering and (d) conventional sintering

Table 2 Sintering studies data obtained in this work in comparison with those reported in the literature

Sintering temperature	Methodology	Reference
1250 °C/15 h	Conventional solid-state reaction route	[14]
1400 °C/5 h	Conventional solid-state reaction route	[46, 47]
1200 °C/6 h	Conventional solid-state reaction route	[48]
1200 °C/12 h	Conventional solid-state reaction route	[49]
1150 °C/2 h	Conventional solid-state reaction route	[50]
1350 °C/6 h	Conventional solid-state reaction route	[15]
1150 °C/2 h	Conventional solid-state reaction route	[51]
1350 °C/10 h	conventional solid-state reaction route	[52]
1350 °C/10 h	Conventional solid state reaction route	[53]
1400 °C/10 h	Conventional solid state reaction route	[54]
950 °C/2 h	Polymeric precursors route	This work

CS conventional sintering

MS microwave sintering

successfully employed in obtaining dense BCGO ceramic. Nonetheless, comparatively, the domestic microwave sintering was found to bear advantages over conventional sintering. Among such advantages include rapid heating, selective material coupling in addition to the enhancement of reaction kinetics. These relevant merits render microwave sintering suitably more attractive for the synthesis of these materials [45]. It is worth noting that the high heating rates are seen to have favored the sintering process through a kinetic effect, i.e., rapid diffusion of minor particles. The high heating rate was found to be at $50\text{ }^{\circ}\text{C min}^{-1}$ (Fig. 3). This implies a sintering temperature of 1370°C —a level regarded significantly lower than those sintering temperatures reported in the literature for BCGO ($1450\text{--}1650\text{ }^{\circ}\text{C}$) as shown in Table 2. Indeed, while this is clearly not a heating rate employed for conventional furnaces, it is attainable in a microwave-assisted heating device, such as a SiC plate, used in this work.

In this work, the FE-SEM images are noted to be of fundamental importance toward understanding the microstructure and densification of the BCGO compounds. The materials sintered by conventional method have an average grain size ranging from 8 to $16\text{ }\mu\text{m}$ while those sintered via the microwave method exhibit a narrow grain size distribution in the range of $6\text{--}10\text{ }\mu\text{m}$ (Fig. 5). These results are in agreement with the reports found in the literature for other

Table 3 Relative density (ρ) of BCGO pellets sintered by conventional and microwave method

Sintering method	BaCe _{0.9} Gd _{0.1} O _{3-δ}		BaCe _{0.8} Gd _{0.2} O _{3-δ}	
Conventional	ρ (%)	RGD* (g cm^{-3})	ρ (%)	RGD* (g cm^{-3})
	91.5	5.84	97.2	6.21
Microwave	90.8	5.74	95.1	6.07

BaCeO₃ theoretical density = 6.38 g cm^{-3}

RGD relative geometric density

ceramic materials. Microwave sintering leads to relatively smaller grain sizes compared to those obtained by conventional sintering mainly as a result of the extremely short sintering time [55].

Nonetheless, the final density of the sintered bodies was found to increase with increase in gadolinium dopant concentration for both sintering methods (Table 3). The densities obtained for conventional and microwave methods were 97.2 and 95.1% respectively for the BCGO doped with 20 mol% of Gd samples.

4 Conclusion

In summary, gadolinium doped barium cerate powder was successfully prepared by the polymeric precursor method. Both conventional and microwave sintering techniques proved to be effective when it comes to obtaining dense ceramic, well sintered bodies in short times and at lower temperatures despite the presence of agglomerated particles in the precursor powders. This study is essentially expected to contribute towards the ongoing efforts to obtain dense ceramic products from nanometric particles for SOFCs based on the application of proton conductors.

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