



Regular article

Electric field-assisted pressureless sintering gadolinium-, yttrium- and samarium-doped barium cerate

R. Muccillo^{a,b,*}, V. Esposito^c, D.Z. de Florio^b, E.N.S. Muccillo^a^a Center of Science and Technology of Materials, Energy and Nuclear Research Institute, S. Paulo, SP 05508-170, Brazil^b Center of Engineering, Modeling and Applied Social Sciences, Federal University of ABC, Santo André, SP 09210-580, Brazil^c Department of Energy Conversion and Storage, Technical University of Denmark, 4000 Roskilde, Denmark

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ABSTRACT

Gadolinium-, yttrium- and samarium-doped barium cerate compounds were sintered either conventionally at 1500 °C or applying an electric field at 1200 °C. The combined results of dilatometry and impedance spectroscopy measurements in electric field-assisted sintered specimens show substantial improvement of the electrical conductivity. Improved grain-to-grain contact and the thermal removal of depleted chemical species due to Joule heating at the space charge region are proposed as the main mechanisms for the increase of both the grain boundary and the bulk electrical conductivities, respectively.

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Even though doped barium cerate and barium zirconate have been proposed to be used as solid electrolytes in solid oxide fuel cells (SOFCs) operating at a temperature lower than the one required in SOFCs with yttria stabilized zirconium oxide, two disadvantages remain to be solved [1–5]: the low sinterability at temperatures available in commercial furnaces and the blocking of protons at grain boundaries. The former has been proposed to be overcome either using sintering aids [6–9], powders produced by chemical routes [10–15] or sinteractive nanosized powder particles, by using thin films prepared by different techniques [16,17]. Recently, the electric field-assisted pressureless sintering (named flash sintering when the shrinkage-consolidation event lasts few seconds, which is the time the electric current pulse traverses the specimen submitted to an electric field) has been used to sinter solid electrolytes at temperatures lower than conventional, producing consolidated bodies without considerable grain growth [18–25]. In short, sintering to near full density is achieved by applying moderate electric fields ($\sim 100 \text{ V cm}^{-1}$) with limiting currents (mA to few A range) to green ceramic pellets upon heating (dynamic process) or isothermally at chosen temperatures below the conventional temperature for sintering. That sintering technique, hereafter flash sintering (FS), is applied here to proton conductors at

temperatures well below the usually required for high densification. Recent compilations of reports show the application of the flash sintering technique to a series of electroceramics, the dependence of the success of the technique on several parameters (particle size, electrical field strength, electric current limit, and temperature), and the proposed mechanisms for sintering during the flash event [26–29]. Renewed attention has been paid recently to the use of new proton conductors in SOFCs, requiring high temperatures and times, for example BZY at 1535 °C for 8 h with NiO sintering aid [30], 1585 °C for 6 h by solid state reaction [30], 1720 °C for 25 by SPS [30], BZDy at 1550 °C for 8 h [31], and more recently BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O₃, sintered at 1600 °C for 24 h [32], and BZY-Ni anode at 1450 °C for 18 h [33]. A preliminary attempt to sinter BaCe_{0.8}Gd_{0.2}O₃ by applying an AC electric field at 910 °C was reported [34]. We describe here experiments on flash sintering three proton conductors synthesized by the same route, BaCe_{0.9}Sm_{0.1}O_{3-δ}, BaCe_{0.9}Gd_{0.1}O_{3-δ} and BaCe_{0.9}Y_{0.1}O_{3-δ}. Specimens with near full density and improved electrical conductivity have been obtained.

BaCe_{0.9}Sm_{0.1}O_{3-δ}, BaCe_{0.9}Gd_{0.1}O_{3-δ} and BaCe_{0.9}Y_{0.1}O_{3-δ} powders were synthesized by the liquid mix technique [35,36] with calcination at 450 °C/1 h for elimination of organic residuals. The experimental setup for sintering green pellets under an electric field consisted on a vertical dilatometer (model 1161, Anter, USA) with the sample holder electrically connected with Pt—Ir leads to a custom-made power supply (70 V, 500–1100 Hz, 0.5 A–5 A current limit control). Further details may be found in previous papers [26,37–42]. The experimental

* Corresponding author at: Center of Science and Technology of Materials, Energy and Nuclear Research Institute, S. Paulo, SP 05508-170, Brazil.
E-mail address: muccillo@usp.br (R. Muccillo).

procedure for isothermal flash sintering consisted on heating the specimen in the dilatometer furnace up to 1200 °C, and applying an electric field up to the occurrence of an electric current pulse; the shrinkage is monitored accurately ($\pm 1 \mu\text{m}$) with the dilatometer gauge. That temperature was chosen for two reasons: first, it is well below the conventional temperature for sintering these compounds to full density (>1500 °C); second, the total electrical resistance is such that a maximum 1 A current may flow with the available voltage power supply. The temperature was monitored with a Pt-Pt10%Rh thermocouple with its tip positioned 5 mm from the specimen. Electric voltage and electric current data were monitored with two Fluke 8050A multimeters and collected with a data logger.

Impedance spectroscopy measurements were carried out with a Hewlett Packard 4192A impedance analyzer. Three cylindrical samples, with their parallel surfaces covered with silver electrodes, were inserted in a sample chamber, positioned inside a programmable furnace. $[-Z''(\omega) \times Z'(\omega)]$ impedance data were collected at 390 °C in the 5 Hz–13 MHz frequency range, 200 mV applied bias, with a special software [43].

X-ray diffraction analyses were performed in a Bruker-AXS D8 Advance diffractometer with a Bragg-Brentano θ - 2θ configuration, $\text{CuK}\alpha$ radiation, 10–90 2θ range, 0.05° step size, 5 s per step. Thermogravimetric analyses of the ceramic powders were carried out in a Netzsch STA 409E under flowing synthetic air, 5 L min^{-1} , from room temperature to 1500 °C. Scanning electron microscopy images were observed in polished and 1400 °C/15 min thermally etched flat surfaces of the sintered pellets with a FEG-SEM Inspect F50 microscope.

The X-ray diffraction patterns of 10 mol% Gd-, Sm- and Y-doped BaCeO_3 powders are similar and correspond to the BaCeO_3 compound (JCPDS 71-2394).

The thermogravimetric analysis of the powders shows 5% mass decrease from room temperature to approximately 750 °C, followed by another 5% decrease up to 1125 °C; the first mass decrease is probably due to the release of physisorbed water, and the second for release of carbon dioxide, known to occur in barium cerate upon handling in the ambient atmosphere. Apparent geometrical densities of the pressed green powders were in the 40–45% of the theoretical density.

Fig. 1 shows the dilatometric curves of the Gd-, Y- and Sm-doped specimens heated to 1500 °C without and 1200 °C with application of an electric field for the flash sintering experiments. The specimens heated to 1500 °C present two shrinkage stages, due to loss of mass, in good agreement with the thermogravimetric analyses. Similar specimens of the doped barium cerates were submitted to flash sintering at 1200 °C. The dilatometric data were collected upon application of 200 V cm^{-1} AC electric fields ($f = 1.1$ kHz) during 5 min at that temperature. The gadolinium-doped sample, Fig. 1a, reaches a 18.4% thickness shrinkage after flash sintering at 1200 °C and 22.5% after conventional sintering to 1500 °C. The samarium-doped sample, Fig. 1b, reaches 20.4% thickness shrinkage after flash sintering at 1200 °C and 33.9% for the specimen conventionally sintered at 1500 °C. The yttrium-doped samples, Fig. 1c, flash sintered at 1200 °C achieved 27.4% thickness shrinkage, a value higher than 15.8%, obtained by heating up to 1500 °C.

Fig. 1 is an evidence that it is possible to sinter doped barium cerate proton conductors at 1200 °C. Even though the specimens are not fully dense, this could be achieved by the proper choice of the electric field, the current limit and the number of current pulses, as described elsewhere [38].

All specimens flash sintered at 1200 °C had their parallel surfaces painted with silver paste and cured at 400 °C for collection of impedance spectroscopy data at 390 °C. The results are shown in Fig. 2. The total electrical resistivity of the specimens flash sintered at 1200 °C is several times lower than in the specimens sintered at 1500 °C without the application of the electric field. Moreover, the impedance

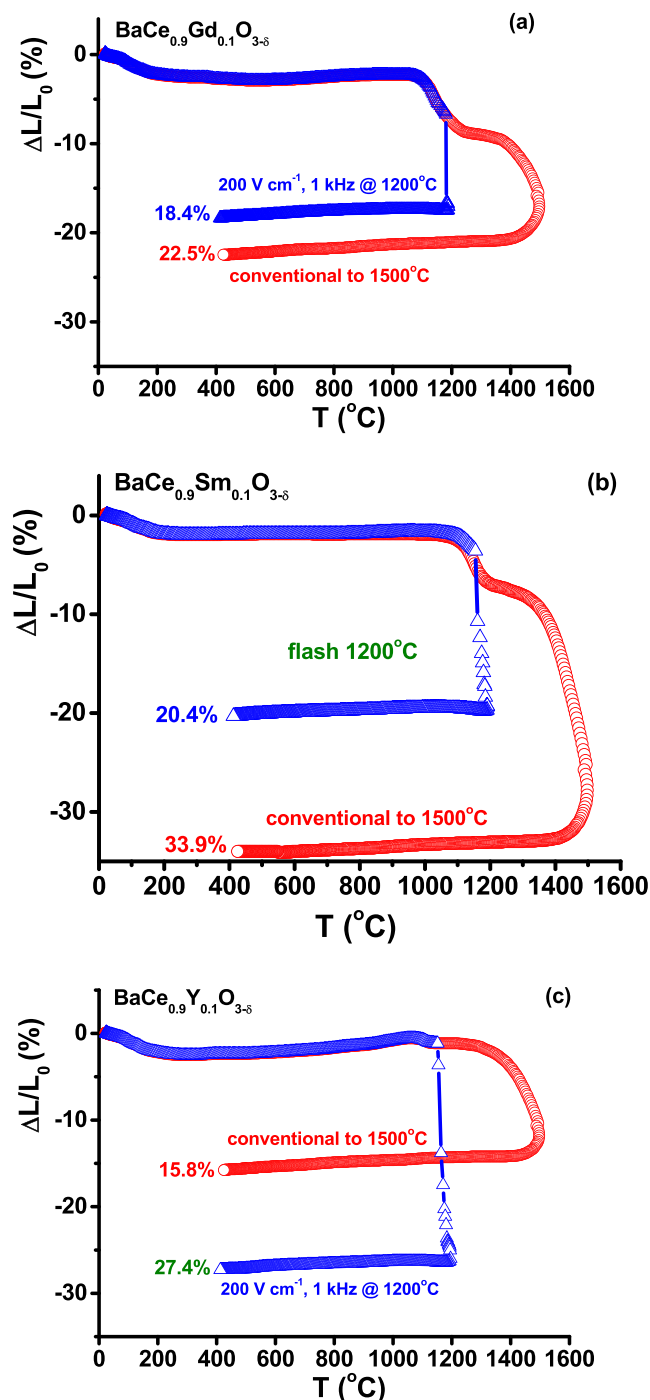


Fig. 1. Dilatometric curves (thickness shrinkage) of (a) $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$, (b) $\text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_{3-\delta}$ and (c) $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ pellets, sintered at 1200 °C by applying 200 V cm^{-1} at 1.1 kHz during 5 min, limiting the current to 5 A. Also shown the dilatometric curves of similar pellets sintered at 1500 °C.

spectra of the flash sintered samples are apparently composed of two semicircles in the measured frequency range, due to intergranular (lower frequency region) and to intragranular (bulk, higher frequency) components of the electrical resistivity (Fig. 2d). The deconvolution of the impedance spectra of Fig. 2d gives the following values for the electrical resistance, normalized for the specimens' dimensions: 6.0 k Ω , 5.2 k Ω and 3.0 k Ω for $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$,

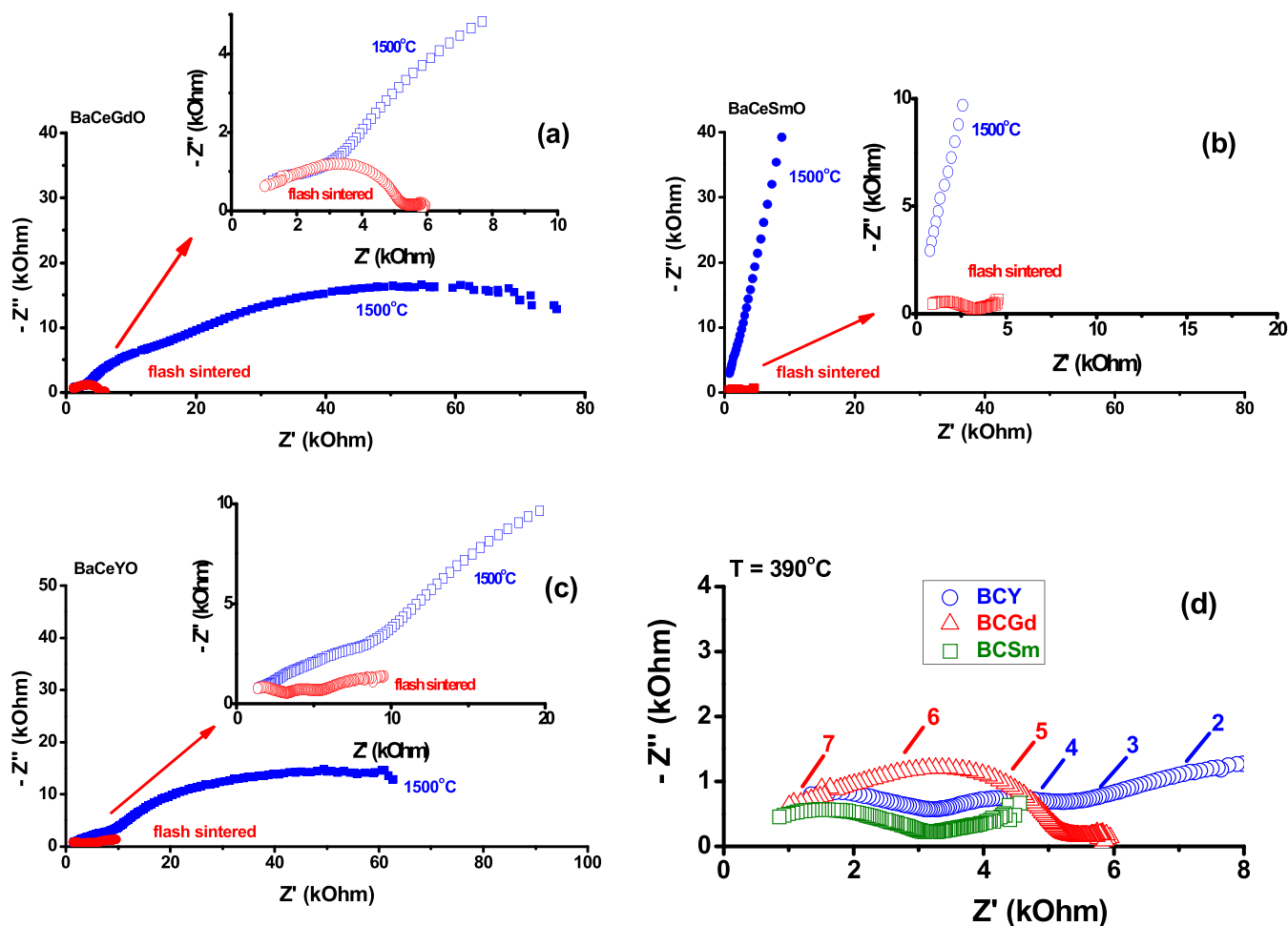


Fig. 2. Impedance spectra in the 5 Hz–13 MHz range of (a) $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$; (b) $\text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_{3-\delta}$; (c) $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ pellets sintered at 1500 °C and flash sintered at 1200 °C; and (d) all samples flash sintered at 1200 °C. Temperature of measurement: 390 °C. Insets: zoom at the high frequency region. Numbers in (d) stand for $\log f$ (f: Hz).

$\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$ and $\text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_{3-\delta}$, respectively. The difference in the electrical resistance is due to the different pore content (see below the SEM analyses).

The main difference in electrical resistivity is apparently in the grain boundary resistivity. It is well known that one of the challenges for obtaining barium zirconate-based proton conductors with electrical resistivity suitable for replacing yttria-stabilized zirconia in solid oxide fuel cell devices remains in decreasing the blocking of protons at the interfaces. One could speculate that the reason for obtaining flash sintered doped barium cerate specimens with high density and low grain boundary resistivity, is the work developed by the electric current pulse at the interfaces of the specimen. The primary reason is evidently the huge increase in the local temperature due to Joule heating, which could improve the grain-to-grain contact and possibly dissolving chemical species, depleted at the space charge region, back to the grains [26]. This would increase the oxide ion vacancy concentration, decreasing the electrical resistivity, as indicated by the impedance diagrams.

Fig. 3 shows scanning electron microscopy micrographs of the flat surfaces of the $\text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_{3-\delta}$, $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$, and $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ flash sintered specimens. Besides presenting high skeletal densities with well-defined neck formation between grains, pores are visible. Apparently, yttrium-doped specimens are more porous than gadolinium-doped specimens, which, by their turn, are more

porous than samarium-doped specimens. This could explain why the total electric resistivity of the three specimens increases according to the sequence (cf. Fig. 2d): $\text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_{3-\delta}$, $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$, $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$. As stated before, further research work should be performed looking for suitable conditions for flash sintering to sinter to full density [38].

Gadolinium, samarium and yttrium-doped barium cerate powders were successfully sintered to near full density by electric field-assisted pressureless sintering at 1200 °C. The grain boundary conductivity of the sintered specimens is highly improved in comparison with the conductivity of specimens conventionally sintered at 1500 °C. Joule heating is suggested as the primary mechanism responsible for modifying the space charge region in such way that diffusion to the bulk of chemical species depleted at the grain boundaries increases the bulk conductivity, and the blocking of protons is inhibited at the interfaces. Further research work is still necessary for defining the optimized conditions for flash sintering proton conductors at temperatures well below the conventional, which could imply in significant manufacture advantage of solid oxide fuel cell devices.

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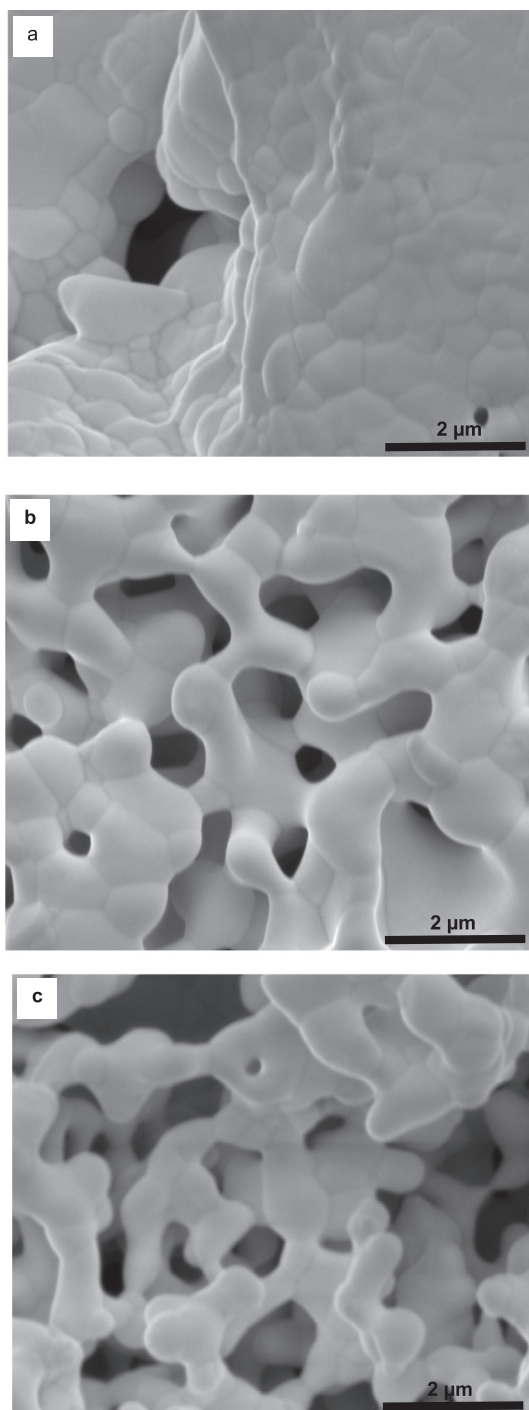


Fig. 3. Scanning electron microscopy micrographs of (a) $\text{BaCe}_{0.9}\text{Sm}_{0.1}\text{O}_{3-\delta}$, (b) $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$, and (c) $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ flash sintered pellets.

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