



# Blocking effect in promising proton conductors based on $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82-x}\text{R}_x\text{O}_{9.8}$ ( $R = \text{Y}^{3+}, \text{Gd}^{3+}, \text{Sm}^{3+}, \text{Nd}^{3+}$ ) ordered perovskites for PC-SOFCs

L.H. Francisco<sup>a</sup>, J.E. Rodrigues<sup>a,b,\*</sup>, W.R. Correr<sup>a</sup>, A.C. Hernandez<sup>a</sup>

<sup>a</sup> Crystal Growth and Ceramic Materials Research Group, São Carlos Institute of Physics, University of São Paulo, CEP 13560-970 São Carlos, SP, Brazil

<sup>b</sup> Optical Spectroscopy and Raman Scattering Research Group, Department of Physics, Federal University of São Carlos, CEP 13565-905 São Carlos, SP, Brazil

## ARTICLE INFO

### Keywords:

$\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9.8}$   
Proton conductor  
Brick-layer  
Space-charge  
Impedance spectroscopy

## ABSTRACT

High proton conductivity and good chemical stability are keys to development of new electrolytes for PC-SOFCs as the next-future energy generation systems. However, the extensive use of new polycrystalline materials as solid electrolytes is still avoided, since the grain boundary response usually leads to a decrease in total conductivity due to electrical blocking effect. Here, we present our results on the space-charge modeling of impedance spectroscopy data obtained for  $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82-x}\text{R}_x\text{O}_{9.8}$  proton conducting ceramics, where  $x = 0, 0.30$  and  $R = \text{Y}^{3+}, \text{Gd}^{3+}, \text{Sm}^{3+}, \text{Nd}^{3+}$  are doping agents. Non-stoichiometric barium calcium niobate perovskites have received much attention as potential solid electrolytes for proton conducting solid oxide fuel cells. We show that despite their increased grain conductivity, the doped ceramics possess Schottky barriers that are higher than those observed for undoped  $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9.8}$ . In view of the space-charge model, proton depletion at the space-charge layer is the reason for the reduction of grain boundary conductivity in the doped compositions. Our findings are important for the understanding of proton conduction mechanisms in polycrystalline materials, which may allow future optimization of new doped electrolytes based on barium calcium niobate perovskites.

## 1. Introduction

Obtaining and optimization of highly efficient materials for energy generation define the state-of-art of the current investigations in materials science and materials chemistry, which are focusing on reducing environmental pollution and prevent global warming [1]. In particular, proton conducting solid oxide fuel cells (PC-SOFCs) are good candidates for future power generation, because they usually lower the SOFCs operating temperatures to intermediate values of 500–700 °C [2,3]. For practical applications, the chemical and mechanical stabilities under  $\text{CO}_2$  and humid atmospheres should be taken into account during the optimization of candidates as PC-SOFCs electrolytes [4]. It is important to emphasize that the high resistivity of grain boundaries (also known as blocking effect) in the electrolytes also prevents their commercialization for intermediate temperature applications, once this feature introduces a decrease in the total conductivity [5–7]. However, until now, few studies in the literature are focused on the origin of the blocking effect in new candidates for PC-SOFCs electrolytes,  $\text{H}_2$  sensors, or steam electrolyzers [8].

From the materials science point of view, most of the studies have been targeted the standard  $\text{BaCeO}_3\text{-BaZrO}_3$  simple perovskites. While

the cerium-based electrolytes have high proton conductivity, zirconates possess good chemical stability in  $\text{CO}_2$ -rich atmospheres. In the last decades, many studies have devoted their attention to optimize the properties of cerate-zirconates, in which rare-earth elements are considered as dopants to create oxygen vacancies in the crystal structure [9]. Otherwise, new compositions are taking place as novel proton conductor electrolytes with satisfactory chemical stability. Among all the reported new ceramic-based electrolytes,  $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82}\text{O}_{9.8}$  (BCN-18) has demonstrated reasonable results concerning both proton conductivity and chemical stability under extreme ambient conditions, making it feasible as electrolyte membrane for PC-SOFCs [10,11].

We should mention the results obtained by Wang et al. on the Y-doped BCN-18, showing that the composition  $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.52}\text{Y}_{0.30}\text{O}_{9.8}$  has an improved proton conductivity of about  $5.3 \times 10^{-3} \text{ Scm}^{-1}$  at 600 °C in comparison with pristine one, besides its salable stability toward carbon dioxide and water (> 24 h resistant at 700 °C) [12]. Zhu et al. doped BCN-18 with  $\text{Ni}^{2+}$  (Ni into Nb sites) in order to improve its sinterability and elevate the proton conductivity, reaching values of  $4.6 \times 10^{-3} \text{ Scm}^{-1}$  at 700 °C [13]. Unlike the simple perovskite with disorder at B-site, BCN-18 is described by an ordered superlattice with the 1:1 stacking sequence of  $-(\text{Ca},\text{Nb})-\text{Nb}-(\text{Ca},\text{Nb})-\text{Nb}-$  along

\* Corresponding author at: Crystal Growth and Ceramic Materials Research Group, São Carlos Institute of Physics, University of São Paulo, CEP 13560-970 São Carlos, SP, Brazil.

E-mail addresses: [lucash.francisco@gmail.com](mailto:lucash.francisco@gmail.com) (L.H. Francisco), [rodrigues.joaobelias@ifsc.usp.br](mailto:rodrigues.joaobelias@ifsc.usp.br), [rodrigues.joaobelias@gmail.com](mailto:rodrigues.joaobelias@gmail.com) (J.E. Rodrigues).

URL: <http://www.ifsc.usp.br> (L.H. Francisco).

<https://doi.org/10.1016/j.ceramint.2018.03.121>

Received 10 January 2018; Received in revised form 10 March 2018; Accepted 13 March 2018

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the  $[111]_c$  planes of the B-site ordered cubic cell. The non-stoichiometric  $\text{Ca}^{2+}$  not only leads to oxygen vacancies, but also allows a modification in the cationic order-type that improves the proton conductivity coming from the ceramic grains [14].

In this paper, we explore the intrinsic origin of the blocking effect in a novel candidate for PC-SOFCs in light of the space-charge model, allowing us to develop a basic understanding of the intrinsic electric response coming from the grain boundaries in proton conducting ceramics based on ordered perovskites. For this purpose, we synthesized new ceramic materials  $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82-x}\text{R}_x\text{O}_{9.8}$ , such that  $x = 0, 0.30$  and  $R = \text{Y}^{3+}, \text{Gd}^{3+}, \text{Sm}^{3+}, \text{Nd}^{3+}$ . The variation of rare earth elements aims the evaluation of both radius and polarizability effects of the doping elements on the electrical properties. We also combined the impedance spectroscopy technique and the brick-layer model to correctly assign the electrical response coming from the grains and grain boundaries. The structural and morphological properties of the ceramic samples were investigated using powder X-ray diffraction, Raman spectroscopy and scanning electron microscopy.

## 2. Theoretical analyses

### 2.1. Brick-layer model

The brick-layer model (BLM) takes grains and grain boundaries as two distinct phases distributed through the material as a network of identical cubes (grains), being separated by boundary phase layers [15,16], as shown in Fig. 1(a). Assuming that electrical current flows only at applied electric field direction, there are two possible conduction branches: (#1) a sequence of long narrow boundaries (parallel grain boundaries) and (#2) a sequence of intercalating grain cubes and thin boundary layers (perpendicular grain boundaries), see in Fig. 1(b). A general model for the material must consider these two paths as parallel circuit branches. Fig. 1(c) displays such a circuit, where each individual phase is modelled by a parallel unit containing  $R||\text{CPE}||\text{C}$  elements. A capacitor is added to the conventional  $R||\text{CPE}$  unit for modeling the high frequency limiting capacitance value, as recently suggested by Hernández et al. [17]. In most cases, due to unfavorable geometry of parallel grain boundaries (gb||) in addition to usual greater boundary phase resistivity, the grain-perpendicular boundary (gb $\perp$ ) branch is the favorable conduction path and the parallel boundary circuit section is usually excluded from the model [18]. Details on BLM can be found in Table S1 of Supplementary information.

### 2.2. Space-charge model

The intrinsic grain boundary conductivity in proton conductors is successfully interpreted in terms of the space-charge model (SCM) [19,20], in which grain boundaries are represented as a positively charged core surrounded by a negatively charged depletion region. The concentration of acceptor dopant is considered constant everywhere outside boundary core (i.e. Mott-Schottky approximation), so that the

negative layer arises only from depletion of positive  $\text{OH}^+$  defects. The potential barrier  $[\Delta\varphi(0) = \varphi(0) - \varphi(\infty)]$  is the intrinsic potential barrier (i.e. Schottky barrier) imposed to the defect transport through grain boundaries. The direct evidence for the presence of such potential barriers on proton conductors has been provided by biased voltage impedance spectroscopy investigations [21,22]. Considering the charge density at the depletion region as being uniform and equal to acceptor dopant volumetric charge density, the equations relating the model parameters to experimentally accessible electrical quantities can be derived [19]. The potential barrier height is directly related to the intrinsic grain and grain boundary conductivities obtained from the brick-layer model by the equation:

$$\frac{\sigma_g}{\sigma_{gb\perp}} = \frac{k_B T}{2e\Delta\varphi(0)} \exp\left[\frac{e\Delta\varphi(0)}{k_B T}\right], \quad (1)$$

where  $\sigma_g$  and  $\sigma_{gb\perp}$  are the grain and grain boundary conductivities;  $\Delta\varphi$  denotes the potential barrier;  $e$ ,  $k_B$  and  $T$  maintain their usual meaning. Here, we denote charge density of dopant atoms by  $\rho_Q$ .  $R$ , being calculated based on the nominal chemical composition of the material. We may define the space-charge layer width  $\lambda^*$  related to the Debye length  $L_D$ , as follows:

$$\lambda^* = 2L_D \left(\frac{e\Delta\varphi(0)}{k_B T}\right)^{\frac{1}{2}}, \quad \text{where } L_D = \left(\frac{\varepsilon \cdot k_B T}{2e \cdot \rho_{Q,R}}\right)^{\frac{1}{2}}, \quad (2)$$

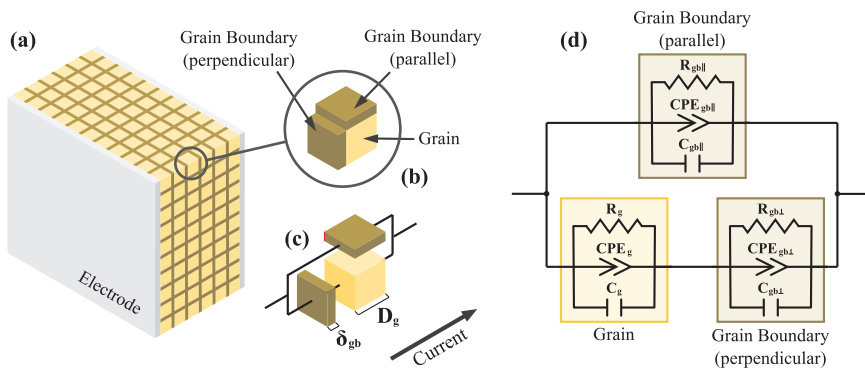
such that  $\varepsilon$  is the dielectric constant. The defect concentration profile  $c_{\text{OH}^+}(r)$  normalized with respect to the defect concentration at the grain's bulk  $c_{\text{OH}^+}(\infty)$  is given by the next expression:

$$\frac{c_{\text{OH}^+}(r)}{c_{\text{OH}^+}(\infty)} = \exp\left[-\frac{1}{4}\left(\frac{r - \lambda^*}{L_D}\right)^2\right]. \quad (3)$$

## 3. Experimental section

### 3.1. Powder synthesis

Powders of  $\text{Ba}_3\text{Ca}_{1.18}\text{Nb}_{1.82-x}\text{R}_x\text{O}_{9.8}$  ( $x = 0, 0.30$  and  $R = \text{Y}^{3+}, \text{Gd}^{3+}, \text{Sm}^{3+}, \text{Nd}^{3+}$ ), hereafter BCN-R system, were synthesized by a conventional solid state reaction. Starting powders of  $\text{BaCO}_3$  (Alfa Aesar; 99.80%),  $\text{CaCO}_3$  (Alfa Aesar; 99.95%),  $\text{Nb}_2\text{O}_5$  (CBMM-Araxá, Brazil; optical degree),  $\text{Y}_2\text{O}_3$  (Alfa Aesar; 99.9%),  $\text{Sm}_2\text{O}_3$  (Alfa Aesar; 99.9%),  $\text{Nd}_2\text{O}_5$  (Fluka; 99.9%) and  $\text{Gd}_2\text{O}_3$  (Alfa Aesar; 99.99%) were stoichiometrically weighted and mixed for 24 h by milling in isopropyl alcohol with zirconia cylinders. The dry mixtures were calcined in air at 1473 K for 5 h and milled in a 4:5 mass fraction solution of isopropyl alcohol in relation to the powder mass. The last calcination and milling steps were repeated to ensure homogeneous phase attainment.



**Fig. 1.** (a) Ceramic material with metallic electrodes on two opposite flat faces. Microstructure is represented as a lattice of cubic grains intercalated with thin grain boundaries, as described by the brick-layer model. (b) The ceramic microstructure is composed of units containing one grain and two boundary units, one perpendicular and one parallel to current direction. (c) Circuit representation of the microstructure in (b) emphasizing the presence of two possible current paths. (d) Equivalent circuit model for the ceramic sample, where each homogeneous phase is represented as a parallel  $R||\text{CPE}||\text{C}$  unit.

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