New Microwave Synthesis of Yttrium-Doped Barium Cerate Nanoparticles Precursor. Phase Transformation During Sintering

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Abstract

Low temperature routes have been developed for the preparation of BaCe₀.₈₅Y₀.₁₅O₂.₉₂₅ (BCY15) in the form of ethanol nanoparticles slurries for use in the central membrane of an original dual cell. Microwave synthesis leads to homogeneous nanoparticles crystalline precursor, as observed by HR-TEM and selected diffraction area (SAD). Single phase yttrium-doped barium cerate perovskites is obtained, as observed by X-ray diffraction, after thermal treatment at 1200°C for 5h. Dynamic temperature X-ray diffraction study revealed that BCY phase growth at 850°C. The BCY15 phase can be obtained after 4h at 950°C. This temperature, lower than those usually used for preparation of BCY, lead to small oxide nanoparticles.

Keywords: Nanoparticles, SOFC; Yttrium-doped Barium cerate, Dynamic temperature X-ray diffraction

1. Introduction

The most simple and popular method for preparation BCY is so-called solid-state reaction method, when the starting compounds (often simple oxides and carbonates) are calcined at temperature higher than 1000°C. Particles obtained using such conventional solid-state reactions are generally very coarse with irregular morphologies. Such high-temperature processes can also easily introduce impurities and reaction phases that can degrade electronic properties of the materials. Moreover, because of the high temperature of the calcinations, the Burumauer-Emmott-Teller (BET) surface area of the resulting BCY powders is generally small, usually less than 10 m²/g.

In addition to the solid state route, several wet chemical techniques like co-precipitation [1-4], modified Pechini process [5, 6] or glycine-nitrate combustion synthesis [7-9] have been employed to obtain ultra fine and more homogeneous powders. Nevertheless, all of these wet chemical techniques require a calcinations step to obtain the desired product.

More recently, Bhowmick et al. [10] have described a solution synthesis method to produce BaCeO₃. This hydrothermal routes require neither a high-temperature calcination (i.e., a high-T heat treatment is not needed to remove volatiles), nor the extensive milling process. Hence, agglomeration of large particles and impurities are both avoided. Depending on the reaction parameters, hydrothermal synthesis can produce different crystal structures and different particle morphologies including cubes, spheres, plates, and cylinders. Hydrothermal routes
have the additional advantages of reproducibility, producing phase-pure materials and allowing excellent control of the stoichiometry. Nevertheless, the XRD of the dried powder (heating at 150°C to evaporate water) contains BaO, BaCeO₃, CeO₂ and BaCO₃. With a 800°C annealing, the powder becomes phase pure BaCeO₃.

Fig. 1 summarizes the general procedure of the liquid-phase synthesis method used in the preparation of BCY with a large surface area. In this method, atomic-level dispersion of the component elements in the precursor solution is essential.

![Diagram of synthesis method](Image)

**Fig 1. Different liquid-phase synthesis method for preparation of BCY.**

### 2. Experimental Methods

#### 2.1. Synthesis method

Yttrium-doped Barium cerate nanopowder dispersions were prepared by original microwave method. Stoichiometric amount of barium, cerium and yttrium salts were mixed in absolute ethanol. Synthesis methods used an original microwave reactor: the RAMO system (French acronym of Reacteur Autoclave MicroOnde). This experimental device is constituted of a microwave applicator associated with an autoclave (Fig. 2). Compared to a domestic oven, the used microwave reactor allows higher electric field strength for the heated sample. By varying the position of a plunger the resonant frequency of the cavity can be controlled and the effective cavity power can be increased by three orders of magnitude. The microwave generator used is a continuous wave system with a power up to 2 kW (2.45 GHz). The autoclave is made with polymer materials which are microwave transparent, chemically inert and sufficiently strong to accommodate the pressure induced. A manometer allows measuring the pressure within the reactor. The system is controlled by pressure. We adjust the microwave power in order to allow constant pressure within the vessel. A pressure release valve incorporated permits to use this experimental device routinely and safely. Furthermore, we can introduce an inert gas such as argon within the reactor to avoid sparking risk with flammable solvents. This experimental device is able to raise the temperature from ambient to 200°C in less than 20 seconds (the pressure is close to 1.2MPa and the heating rate is close to five degrees per second).
For each experiment, 25mL of the metal salts precursor ethanol solution is placed in a Teflon flask inserted within a polyetherimide flask. This reactor was quickly sealed under argon pressure introduced (0.5 MPa). The RAMO treatment was decomposed in two steps. The first step correspond to the heating ramp, the microwave power is applied until the pressure reaches a threshold value. Isothermal step is obtained by adjusting microwave power to maintained required pressure threshold for few minutes. The obtained slurries were collected and concentrated up to desired concentration and stored under inert atmosphere before characterisation.

2.2. Characterization

Transmission electron microscopy (TEM) studies were carried out on JEOL JEM-2100 TEM with LaB6 source operating at accelerating voltage of 200kV. Ultrathin windowed energy-dispersive X-ray spectrometer (EDS) attached to the TEM microscope was used to determine the chemical composition of sample. For TEM experiments samples were prepared by dipping a 300-mesh carbon film coated copper grid into a vial containing the synthesized dilute pre-sonicated BCY ethanol dispersion, with subsequent solvent evaporation in contact with ambient air at room temperature.

X-ray powder diffraction (XRD) measurements were performed with a brucker-AXS D8 Advance diffractometer (Cu-Kα radiation, λ = 0,154051 nm) using a super speed VANTEC-1 detector. Dynamic temperature X-ray diffraction studies have been performed with a MRI-Basic temperature chamber under Helium flow. The following method has been used to simulate the sintering of BCY: a 5°C.min⁻¹ heating rate over a temperature range from 30 to 1200°C (950°C) was
followed by a 5 hours 1200°C (950°C) isotherm. The angular range (22° < 2θ < 52°) was chosen in order to identify the compounds that can be observed during thermal treatment. Measurements were made from 22° to 52° (2θ) with a step size of 0,026° and 0,4 per step. This results in a total measurement time of only 10 minutes corresponding to a temperature variation of 50°C.

Powder were extracted from ethanol and pressed into pellets by colled pressing (2 T at room temperature for 1 mn). They were sintered at 1200°C for 5h with ramp rate of 5°C.min⁻¹. The density of the pellets was determined by measuring the geometric dimensions and weighing the pellets after sintering.

Atomic element ratio was determined with a VARIAN Vista-Pro inductively coupled plasma optical emission spectrometer.

3. Results and discussion
3.1. Characterization of the precursor nanoparticles

The microwave reaction method present many advantages such as homogeneity, control of stochiometry, short heating time and temperature, production of uniform nanoparticles of size in the nanometer range at low cost. Uniform dispersion with off white to light yellow colour is obtained and can easily used for tape casting. Dispersed Nanoparticles can sometimes settle upon storage, because of agglomeration. These agglomerates can be dispersed using ultrasonic treatment.

The High Resolution Transmission electronic Microscopy (HR-TEM) morphological analyses were performed on the ethanol BCY dispersion and reveal small crystalline nanoparticles with size close to 5nm (Fig. 3).

![Figure 3. HR-TEM micrograph of BCY15 nanopowder obtained by microwave synthesis.](image)

The Transmission Electronic Microscopy Selected Area Diffraction (TEM-SAD) has been performed on raw powder. The diffraction pattern is described by the Fig
4. The selected area diffraction pattern indicates the presence of crystalline nanoparticles. Analysis of diffraction pattern on selected area clearly reveals the presence of three distinct halos (A, B, C) and a broad one (D). The characteristic distance determination is difficult due to a strong broadening and asymmetric intensity. This phenomenon is probably due to the very small size of particles.

![Fig. 4. Diffraction pattern (a) of the selected area symbolized by the black circle on the TEM image.](image)

The Table 1 shows the estimated distance values on TEM-SAD pattern and their possible assignation in relation to BCY and YDC crystallographic structures:

<table>
<thead>
<tr>
<th>Interval / point</th>
<th>Mesured distance on SAD pattern (nm)</th>
<th>ICDD N° 01-075-0175</th>
<th>ICDD N° 01-07-6751</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[hkl]</td>
<td>Distance (nm)</td>
<td>[hkl]</td>
</tr>
<tr>
<td>A</td>
<td>0,32-0,30</td>
<td>[111]</td>
<td>0,312</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>0,22-0,19</td>
<td>[220]</td>
<td>0,191</td>
</tr>
<tr>
<td>C</td>
<td>0,18-0,15</td>
<td>[311]</td>
<td>0,163</td>
</tr>
<tr>
<td>1</td>
<td>0,31</td>
<td>[111]</td>
<td>0,312</td>
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<tr>
<td>2</td>
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<td>Not attributed</td>
<td>[202] , [040]</td>
</tr>
<tr>
<td>3</td>
<td>0,16</td>
<td>[311]</td>
<td>0,163</td>
</tr>
</tbody>
</table>

The error on positions induces a doubt on the identification phase for the raw product. In the case of interval values (A, B, C) it is possible to identify BCY phase. However, if we consider a local point placed on the maximum intensity of each halo (1, 2, 3), it seems to correspond to YDC phase. However, the absence of 0,27 nm characteristic distance of YDC assumes that the raw product is mainly constituted by BCY.
3.2. Temperature X-ray diffraction: simulation of sintering

Several researchers have reported the formation of barium hydroxide and barium carbonate due to natural reactivity of BCY with water and carbon dioxide. Moreover, some studies have shown that BCY could be a potential carbon dioxide capturing agent. According to literature, BCY can absorb 0.13 g of carbon dioxide per ceramic gram in the temperature range 700-1000°C. During this reaction, BCY would be partially transformed into YDC. This natural behavior of micrometer particles is strongly enhanced for nano-sized powder with large specific area. During process it is necessary to avoid or limit drastically contact with water and carbon dioxide. The first step will be moisture adsorption. Secondly, water adsorption upon BCY will produce barium hydroxide. Finally, barium hydroxide will react with carbon dioxide to lead barium carbonate.

BCY15 nanopowder precursor was obtained by extracting ethanol solvent with rotary evaporator and dried under vacuum over the night. XRD have been performed on the raw nanopowder Fig. 5. Due to the high surface area, nanopowder can easily react with air moisture. This phenomenon can explain the presence of barium hydroxide hydrate phase (Ba(OH)$_2$.H$_2$O, ICDD N° 00-026-0154). Broadened diffraction peaks are characteristic of nanosized crystallized particles. However the broadening limits the determination of the crystallographic phase.

![XRD diagram of raw BCY15 nanoparticles precursor.](image)

As it is shown on the Fig. 6, several crystallographic phases can be observed during the heating ramp. The arrow shows the presence of scattering peak associated to the MRI temperature chamber. Up to 280°C, only barium hydroxide phases are clearly identified. At this temperature range barium hydroxide hydrate crystals are loosing H$_2$O molecules to transform in barium hydroxide (ICDD N° 01-073-8492).
While the experiment was performed under helium it seems surprising to observe barium carbonate appearance (ICDD N° 01-071-2394) for temperature above 300°C. This appearance could be correlated with the presence of ethanol molecule chemisorbed on the nanoparticles surfaces. At this temperature, these molecules could be decomposed to form carbon dioxide. For temperatures above 680°C, growth of yttrium-doped cerate can be observed (ICDD N° 01-075-0174). The presence of this crystallographic is in accordance with the stochiometric lack of Barium. Finally, BCY15 (ICDD N° 01-070-6743) nanocrystallites begin to growth as temperature became higher than 930°C. At 1100°C, a pure BCY15 phase can be observed.

In the aim to reduce the sintering process and to obtain small BCY15 nanoparticles with high surface area, it seems important to study the kinetics of BCY15 crystallite growth at 950°C. An in situ isothermal XRD analyses revealed that single BCY15 crystallographic phase is observed after 4 hours at 950°C (Fig. 7).
During the isothermal treatment, the phases and BaCO$_3$ YDC rearranges by diffusion within the material by promoting the growth phase BCY. It seems that the size of nanoparticles BCY evolve over after 4 h of treatment. However, further investigation is needed to determine the average size of crystallites. In fact, during the treat thermal shrinkage of the sample is observed. This variation explains the dimensional shift of the diffraction peaks from the theory.

4. Conclusion

The objective of this research was to investigate the potential of environmentally friendly microwave synthesis for the preparation of proton conducting BaCe$_{0.85}$Y$_{0.15}$O$_{2.925}$ in the form of nanoparticles slurries adapted for tape casting. The association of elemental analysis, transmission microscopy and dynamic temperature X-ray diffraction provides converging results indicating the presence of nanosized single BCY15 crystallites after few hours at 950°C. These slurries could be used to enhance densification during sintering by combining them with higher size of BCY particules. The ultra small particles size of the BCY15 precursor crystallite and their surface reactivity could be used to generate porous membrane. Analysis to measure crystallite size and specific surface are in progress.

Acknowledgements

The research leading to these results has received funding from European Community’s Seventh Framework Programme (FP7/2007-2013) under grant agreement No 213389. Remy Chassagnon, and Marion Technologie are acknowledged with thanks, for the HR-TEM measurement and Marion technologies and ICP measurement respectively.
References