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1 **Continuous hydrothermal synthesis in supercritical** 2 **conditions as a novel process for the elaboration of Y-doped** 3 **BaZrO₃**

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10 **Abstract:** The present work describes a novel process for the elaboration of a ceramic material.
11 Y-doped barium zirconate, an electrolyte material for Protonic Ceramic Fuel cell, was synthesized
12 by a continuous hydrothermal process in supercritical conditions (410°C/30.0MPa) using nitrate
13 precursors and NaOH reactants. The use of supercritical water allowed the formation of particles of
14 about 50 nm in diameter with a narrow size distribution. X-Ray Diffraction examination revealed
15 that a major perovskite phase with few BaCO₃ and YO(OH) impurities was obtained. BaCO₃ is
16 assumed to form due to faster kinetics than Y-doped BaZrO₃ resulting in a Ba-deficient perovskite
17 phase. The Ba-deficiency limits the incorporation of yttrium into the perovskite structure. However,
18 a thermal treatment at 1000 °C for 1 hour allows to homogenize the composition and thus to obtain
19 the compound Ba_{1.01}Zr_{0.85}Y_{0.15}O_{3-δ}.

20 **Keywords:** Hydrothermal synthesis; Protonic Ceramic Fuel Cell; Nanoparticles; Supercritical
21 water; Y-doped BaZrO₃.

22 **1. Introduction**

23 Finding new clean and efficient ways to generate energy has become a major global challenge.
24 For a few years now, Protonic Ceramic Fuel Cells (PCFCs) have attracted much attention in the field
25 of hydrogen energy. Contrary to Solid Oxide Fuel Cells that operate at a temperature above 600 °C
26 and where the oxygen ions are the charge carriers, PCFCs use protons. Indeed, the lower activation
27 energy of proton diffusion compared to that of the oxygen ion allows to decrease the operating

28 temperature down to the 400 – 600 °C range[1]. Among the different electrolyte materials for
29 PCFCs, BaCeO₃ and BaZrO₃ have attracted much attention [2–4].

30 BaCeO₃-based oxides are currently the most commonly chosen electrolyte material for PCFC
31 [5,6]. It is generally reported that doped-BaCeO₃ exhibits the highest protonic conductivity among
32 the perovskite-type materials [7–9]. However, BaCeO₃-based perovskites exhibit low stability in
33 H₂O and/or CO₂ containing atmosphere which limits their practical application [10,11]. On the
34 contrary, doped BaZrO₃ exhibits excellent chemical stability [12]. The substitution of zirconium by
35 yttrium allows to achieve acceptable electrical conductivity up to 10⁻³ S.cm⁻¹ [13,14]. However, the
36 highly refractive nature of BaZr_{1-x}Y_xO_{3-δ} (noted BZY) leads to the requirement of a high synthesis
37 temperature (1400 °C) for the classical solid state reaction method and to an even higher (1600 –
38 1700 °C) sintering temperature [15,16].

39 In this work, a continuous hydrothermal process developed at the ICB laboratory is proposed
40 to elaborate the electrolyte material [17]. The supercritical hydrothermal synthesis of metal oxide
41 particles using a continuous flow reactor was first proposed by Adschiri *et al.* in 1992 [18]. This
42 process presents several advantages such as a precise control of the morphology and the size of the
43 particles with a narrow size distribution [19–21]. Furthermore, in supercritical water, inorganic
44 compounds become insoluble leading to the formation of hydroxide nuclei which are immediately
45 dehydrated to form ultrafine particles [22]. Another important advantage of using supercritical
46 water with a continuous flow is the short reaction time leading to the possible formation of
47 metastable and highly doped structures [23,24].

48 The synthesis of BaZrO₃ by the continuous hydrothermal process was investigated by several
49 groups in the past decade. For example, Aimable *et al.* studied the influence of the nature of the
50 precursors, the pH and the temperature on the synthesis of BaZrO₃ [25]. Yoko *et al.* studied the
51 formation mechanism of BaZrO₃ in supercritical water. They suspected the formation of
52 Ba-deficient particles with a shell of ZrO(OH) at the early stage of the precipitation followed by an
53 uptake of Ba²⁺ up to Ba/Zr=1 [26]. In 2016, the same group used *in situ* X-ray diffraction to study
54 and support the previous mechanism [27].

55 However, few studies focus on doped BaZrO₃ material elaborated by this method, and, to the
56 authors' knowledge, no studies on Y-doped BaZrO₃ have been conducted. Then, this work aims to

57 investigate the feasibility of the elaboration of $\text{BaZr}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ by supercritical hydrothermal process
58 using a continuous flow reactor.

59 2. Materials and Methods

60 2.1. Continuous process

61 The continuous process can be used up to 600 °C/35.0 MPa. Indeed, for water, the critical
62 temperature/critical pressure values are 374 °C/22.1 MPa, this set-up can work in supercritical
63 conditions. For the experiments, the syntheses were carried out at 410 °C/30.0 MPa. A solution of
64 metallic precursors ($\text{Ba}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ purchased from Sigma-Aldrich)
65 is prepared by following the stoichiometry of the target composition by dissolution in deionized
66 water and homogenized with an ultrasonic rod, the concentration is $5 \times 10^{-2} \text{ mol L}^{-1}$ for Ba^{2+} , 4×10^{-2}
67 mol L^{-1} for Zr^{4+} and $1 \times 10^{-2} \text{ mol L}^{-1}$ for Y^{3+} . A second solution composed of sodium hydroxide at
68 $3 \times 10^{-1} \text{ mol L}^{-1}$ was employed in order to avoid the formation of ZrO_2 [25]. **Figure 1** shows the
69 scheme of the continuous set-up. Container (a), at the beginning of the process, holds the aqueous
70 solution of metal cations, container (b) holds the solution of sodium hydroxide and the third
71 container (c) holds the distilled water. The reactor consists of a “pipe to pipe” cylinder with a total
72 volume of 25 mL, the inner diameter of the external pipe is 10 mm. Pressurized solutions (a) and
73 (b) are brought to the reactor inlet at room temperature by high-pressure pumps. Pressurized
74 demineralized water is pre-heated and brought counter-currently through the internal pipe of the
75 reactor so that the three solutions meet at the mixing zone. The resulting solution is evacuated
76 through the external pipe where the reactions leading to the formation of metal oxides take place.
77 The flow rate of the three solutions is set to around 10 mL min^{-1} per solution, the final flow
78 measured at the end of the set-up (after the back pressure regulator) varies between 30 and 35
79 mL.min^{-1} . The residence time into the reactor under supercritical conditions is of the order of few
80 seconds (determined by Computational Fluid Dynamics calculations) [28]. At the reactor outlet, a
81 cooling system stops the germination and growth stages. A filtration system at the end of the device
82 captures the agglomerated particles that are added to the suspension obtained after the
83 back-pressure regulator. The particles sediment at the bottom of the beaker, the surfactant is
84 siphoned off and distilled water is added to wash the particles. This operation is repeated until a

85 neutral pH is obtained. The supernatant water is siphoned off one last time and the suspension is
86 dried in an oven at 80 °C for three days to obtain a powder.

87 2.2. Characterization methods

88 X-Ray Diffraction (XRD) analysis was conducted on a Bruker D2 Phaser coupled with linear
89 detector Lynxeye_XE_T using Cu K α radiation. The obtained XRD pattern was refined by the
90 Rietveld method using the Fullprof software. The microstructure was investigated by transmission
91 electron microscopy (TEM) on a ThermoFisher FEI Tecnai F20. The chemical composition was
92 analyzed by scanning electron microscopy (SEM) on a Hitachi SU1510 coupled with a Bruker
93 XFlash6110 energy-dispersive X-ray (EDX) analyzer. The collected peaks for EDX quantification
94 were the L-series of Ba, Zr and Y and the K-series of O. EDX investigations were conducted on 16
95 different agglomerates with an area of measurement from 2.5 $\mu\text{m} \times 2.5\mu\text{m}$ to 5 $\mu\text{m} \times 5 \mu\text{m}$. The
96 Brunauer, Emmett and Teller (BET) measurement was carried out on a Micromeritics TriStar 3020.
97 Particle size distribution (PSD) was evaluated using the Dynamic Light Scattering method using Mie
98 theory calculation with a Malvern Microsizer 2000 laser granulometer coupled with a hydro
99 2000MU dispersion unit using ultrasound.

100 3. Results and discussion

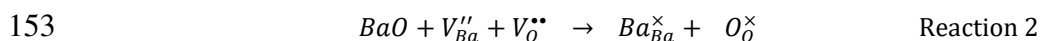
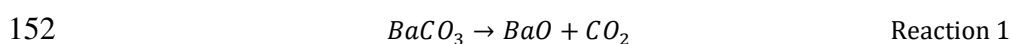
101 Among the Y-doped BaZrO₃ materials, BaZr_{0.8}Y_{0.2}O_{3- δ} appears to be the best composition. The
102 protonic conductivity increases with the Y content up to a substitution of 20 % before decreasing
103 due to structural distortion and proton trapping [29,30]. Thus, BaZr_{0.8}Y_{0.2}O_{3- δ} was the target
104 composition. The chemical reaction yield varies from 60.5 % to 70 % with an average value of 66.5
105 %, the productivity depends on the final flow measured after the back pressure regulator and
106 varies from 5.5 to 6.8 g.h⁻¹, about 23.5 g was produced per synthesis.

107 **Figure 2** shows the volume and number PSD of the synthesized powder. The volume PSD
108 (Figure 1.a) exhibit a quadrimodal distribution with mean sizes at around 0.1 μm , 1.7 μm , 14 μm
109 and 210 μm . The obtained D₁₀, D₅₀ and D₉₀ are 0.817 μm , 4.570 μm and 35.73 μm respectively
110 suggesting that the elementary grains are highly agglomerate. **Figure 3** shows the TEM micrograph
111 of the synthesized powder. As suggested by the PSD analysis, the particles with a nearly spherical
112 morphology are agglomerated. The particle size varies from 10 nm to 315 nm on this micrograph
113 with a median value of 48 nm (evaluation on 50 particles).

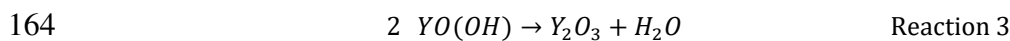
114 The X-ray diffractogram of the obtained powder is shown in **Figure 4**. The major phase
115 obtained has a perovskite cubic structure with Pm-3m space group. BaCO₃, with an orthorhombic
116 Pnma structure, and YO(OH), with a monoclinic P2₁/m structure as secondary phases were
117 detected. Rietveld refinement was performed on the diffractogram, the determined phase
118 percentages are 86.2, 10.6 and 3.1 wt% for BZY, BaCO₃ and YO(OH) respectively. The average
119 crystallite size of the perovskite phase was evaluated from the integral width of the diffraction
120 peaks and is 53 nm. This value is in agreement with the 48 nm obtained from TEM analysis and
121 with the 47.3 ± 0.2 nm calculated from the 20.74 ± 0.06 m² g⁻¹ specific surface area obtained by BET
122 measurement. The refined lattice parameter for the perovskite cubic phase is 4.2015 Å, this value is
123 lower than those reported in the literature for BaZr_{0.8}Y_{0.2}O_{3-δ} suggesting that a part of Y is not in the
124 perovskite phase leading to the formation of YO(OH). As a comparison, Sun *et al.* obtained a lattice
125 parameter of 4.2048 Å for BaZr_{0.8}Y_{0.2}O_{3-δ} prepared by combustion method, Nuñez et al. obtained a
126 lattice parameter of 4.2067 Å for BaZr_{0.8}Y_{0.2}O_{3-δ} prepared by a modified Pechini method and Sazinas
127 *et al.* obtained a lattice parameter of 4.2151 Å for BaZr_{0.8}Y_{0.2}O_{3-δ} prepared by spray pyrolysis and
128 sintered at 1600 °C [31–33]. In order to investigate the origin of lattice parameter deviation, a
129 comparison with undoped BaZrO₃ elaborated by the same method was carried out. The refined
130 lattice parameter is 4.1939 Å, this value agrees well with the 4.1930 Å and the 4.1943 Å obtained by
131 the Nuñez group and the Akbarzadeh group [32,34]. Then, this synthesis method does not appear
132 to particularly generate defects or nano-size effects that affect the lattice parameter. Moreover, the
133 increase in the lattice parameter for Y-doped BaZrO₃ compared to the non-doped sample well
134 evidence the Y doping. However, the amount of Y cannot be quantified by XRD since the synthesis
135 route implement several defects or structural distortions that affect the lattice parameter value, for
136 example, values of lattice parameter for BaZr_{0.9}Y_{0.1}O_{3-δ} differ from 4.193 Å to 4.2101 Å [33,35–38].

137 In order to determine the composition of the BZY powder as-synthesized, EDX investigations
138 were conducted on several agglomerates. Ba, Zr, Y and O elements were detected, for the following
139 interpretation, Ba is assumed to belong to the A-site of the perovskite while Zr and Y are supposed
140 to occupy the B-site of the perovskite. **Figure 5** shows a) the obtained A-site/B-site ratios and b)
141 the obtained Y/(Zr+Y) ratios and the corresponding number of agglomerates per interval. The
142 as-synthesized powder exhibits a wide range of A-site/B-site ratio, from 0.70 to 1.33, with a strong
143 tendency for the Ba-deficient composition. In order to homogenize the composition, a heat

144 treatment at 1000 °C for 1 hour was applied to the powder. The resulting distribution of
 145 A-site/B-site ratio is narrower, the lower value is 0.92 and the biggest value is 1.08 with an average
 146 value equal to 1.01. Then, the thermal treatment at 1000°C effectively homogenizes the
 147 composition. Moreover, a study of Haile group showed that BaCO₃ decomposition leads to the
 148 compensation of the Ba sub-stoichiometry during sintering [39]. Since BaCO₃ decomposition
 149 (reaction 1) occurs at around 1000 °C [40], it can reasonably be assumed that the increase of the
 150 A-site/B-site ratio in the annealed powder is due to the Ba uptake from BaCO₃. The integration of
 151 Ba in the BZY structure is described in Kröger – Vink notation in reaction 2.



154 The Y/(Zr+Y) ratio values of the as-synthesized powder cover an interval of 0.08 to 0.25 with
 155 an average value of 0.14, this ratio is lower than the expected 0.20. Yamazaki *et al.* and Magrez *et al.*
 156 have shown that yttria exsolution in Ba-deficient BZY compounds during sintering is due to the Ba
 157 sub-stoichiometry [41,42]. It can then be assumed that, in hydrothermal synthesis, the
 158 Ba-deficiency caused by the kinetics of the BaCO₃ formation faster than the BZY formation hinders
 159 the incorporation of more than 14 % of Y in the BZY structure. After thermal treatment, the
 160 distribution of Y/(Zr+Y) is substantially the same as before, covering an interval from 0.07 to 0.24
 161 with an average value of 0.15. Because of the high occupancy rate of the B-site of the perovskite,
 162 yttrium from YO(OH) cannot integrate the perovskite structure and react at 450 °C to form Y₂O₃
 163 according to reaction 3 [43]:



165 4. Conclusions

166 The hydrothermal synthesis of BaZr_{1-x}Y_xO_{3-δ} was carried out in supercritical water (410
 167 °C/30.0 MPa) using a continuous flow reactor. This process allows the elaboration of nanoparticles
 168 of about 50 nm in diameter with great productivity (5.5 – 6.8 g h⁻¹), an average chemical reaction
 169 yield of 66.5 % and high reproducibility. XRD characterization revealed the presence of BaCO₃ and
 170 few YO(OH) impurities. It is assumed that BaCO₃ formation occurs due to faster kinetics compared
 171 to that of BZY formation. EDX study showed the obtaining of highly Ba-deficient perovskite and a
 172 substitution rate of Zr by Y of about 14%. However, a thermal treatment at 1000 °C for 1 hour

173 allowed the homogenization of the composition resulting in a $\text{Ba}_{1.01}\text{Zr}_{0.85}\text{Y}_{0.15}\text{O}_{3-\delta}$ perovskite phase.
174 In summary, this continuous hydrothermal synthesis in supercritical conditions is highly promising
175 and extensive research on controlling the synthesis parameters would greatly broaden the
176 possibilities for elaborating advanced ceramic materials at low temperature.

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181 **Conflicts of Interest:** The authors declare no conflict of interest.

182 References

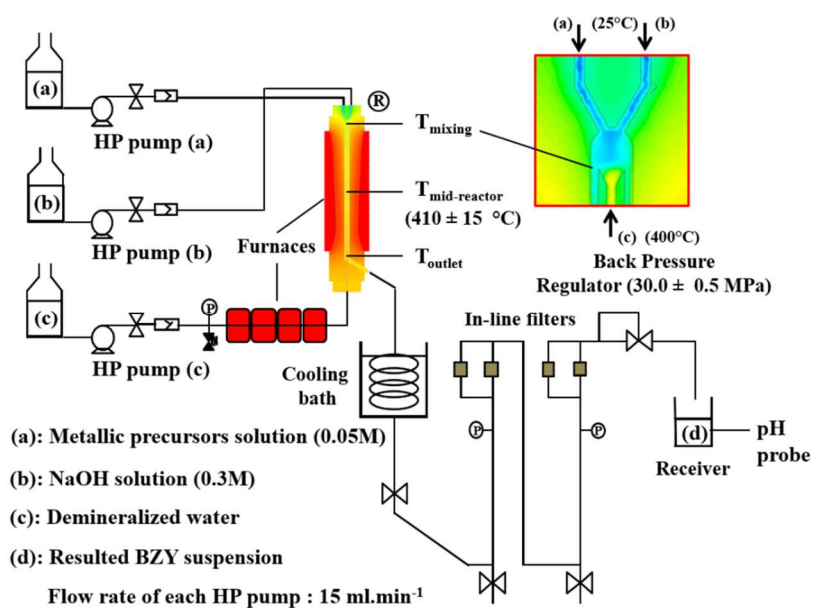
- 183 [1] Y. Meng, J. Gao, Z. Zhao, J. Amoroso, J. Tong, K.S. Brinkman, Review: recent progress in
184 low-temperature proton-conducting ceramics, *J Mater Sci.* 54 (2019) 9291–9312.
185 <https://doi.org/10.1007/s10853-019-03559-9>.
- 186 [2] S. Hossain, A.M. Abdalla, S.N.B. Jamain, J.H. Zaini, A.K. Azad, A review on proton conducting
187 electrolytes for clean energy and intermediate temperature-solid oxide fuel cells, *Renewable
188 and Sustainable Energy Reviews.* 79 (2017) 750–764.
189 <https://doi.org/10.1016/j.rser.2017.05.147>.
- 190 [3] A. Nowick, High-temperature protonic conductors with perovskite-related structures, *Solid
191 State Ionics.* 77 (1995) 137–146. [https://doi.org/10.1016/0167-2738\(94\)00230-P](https://doi.org/10.1016/0167-2738(94)00230-P).
- 192 [4] H. Dai, H. Kou, H. Wang, L. Bi, Electrochemical performance of protonic ceramic fuel cells with
193 stable BaZrO_3 -based electrolyte: A mini-review, *Electrochemistry Communications.* 96
194 (2018) 11–15. <https://doi.org/10.1016/j.elecom.2018.09.001>.
- 195 [5] X. Xu, L. Bi, Proton-conducting electrolyte materials, in: *Intermediate Temperature Solid
196 Oxide Fuel Cells*, Elsevier, 2020: pp. 81–111.
197 <https://doi.org/10.1016/B978-0-12-817445-6.00003-X>.
- 198 [6] L. Bi, Z. Tao, C. Liu, W. Sun, H. Wang, W. Liu, Fabrication and characterization of easily
199 sintered and stable anode-supported proton-conducting membranes, *Journal of Membrane
200 Science.* 336 (2009) 1–6. <https://doi.org/10.1016/j.memsci.2009.03.042>.
- 201 [7] K.D. Kreuer, Proton-Conducting Oxides, *Annual Review of Materials Research.* 33 (2003) 333–
202 359. <https://doi.org/10.1146/annurev.matsci.33.022802.091825>.
- 203 [8] K.H. Ryu, S.M. Haile, Chemical stability and proton conductivity of doped BaCeO_3 – BaZrO_3
204 solid solutions, *Solid State Ionics.* 125 (1999) 355–367.
205 [https://doi.org/10.1016/S0167-2738\(99\)00196-4](https://doi.org/10.1016/S0167-2738(99)00196-4).
- 206 [9] S. Wang, J. Shen, Z. Zhu, Z. Wang, Y. Cao, X. Guan, Y. Wang, Z. Wei, M. Chen, Further
207 optimization of barium cerate properties via co-doping strategy for potential application as
208 proton-conducting solid oxide fuel cell electrolyte, *Journal of Power Sources.* 387 (2018) 24–
209 32. <https://doi.org/10.1016/j.jpowsour.2018.03.054>.

- 210 [10] H. Matsumoto, Y. Kawasaki, N. Ito, M. Enoki, T. Ishihara, Relation Between Electrical
211 Conductivity and Chemical Stability of BaCeO₃-Based Proton Conductors with Different
212 Trivalent Dopants, *Electrochemical and Solid-State Letters*. 10 (2007) B77.
213 <https://doi.org/10.1149/1.2458743>.
- 214 [11] W. Münch, Proton diffusion in perovskites: comparison between BaCeO₃, BaZrO₃, SrTiO₃,
215 and CaTiO₃ using quantum molecular dynamics, *Solid State Ionics*. 136–137 (2000) 183–189.
216 [https://doi.org/10.1016/S0167-2738\(00\)00304-0](https://doi.org/10.1016/S0167-2738(00)00304-0).
- 217 [12] J.-H. Kim, Y.-M. Kang, M.-S. Byun, K.-T. Hwang, Study on the chemical stability of Y-doped
218 BaCeO_{3-δ} and BaZrO_{3-δ} films deposited by aerosol deposition, *Thin Solid Films*. 520 (2011)
219 1015–1021. <https://doi.org/doi:10.1016/j.tsf.2011.08.013>.
- 220 [13] E. Fabbri, L. Bi, D. Pergolesi, E. Traversa, Towards the Next Generation of Solid Oxide Fuel
221 Cells Operating Below 600 °C with Chemically Stable Proton-Conducting Electrolytes,
222 *Advanced Materials*. 24 (2012) 195–208. <https://doi.org/10.1002/adma.201103102>.
- 223 [14] D. Yun, J. Kim, S.-J. Kim, J.-H. Lee, J.-N. Kim, H. Yoon, J. Yu, M. Kwak, H. Yoon, Y. Cho, C.-Y. Yoo,
224 Structural and Electrochemical Properties of Dense Ytria-Doped Barium Zirconate Prepared
225 by Solid-State Reactive Sintering, *Energies*. 11 (2018) 3083–3099.
226 <https://doi.org/10.3390/en11113083>.
- 227 [15] L. Bi, E. Traversa, Synthesis strategies for improving the performance of doped-BaZrO₃
228 materials in solid oxide fuel cell applications, *J. Mater. Res.* 29 (2014) 1–15.
229 <https://doi.org/10.1557/jmr.2013.205>.
- 230 [16] F.J.A. Loureiro, N. Nasani, G.S. Reddy, N.R. Munirathnam, D.P. Fagg, A review on sintering
231 technology of proton conducting BaCeO₃-BaZrO₃ perovskite oxide materials for Protonic
232 Ceramic Fuel Cells, *Journal of Power Sources*. 438 (2019) 226991.
233 <https://doi.org/10.1016/j.jpowsour.2019.226991>.
- 234 [17] D. Aymes, M. Ariane, F. Bernard, H. Muhr, F. Demoisson, Counter-current flow reactor with
235 heat transfer for hydrothermolytic synthesis, WO 2011010056A1, 2011.
- 236 [18] T. Adschiri, K. Kanazawa, K. Arai, Rapid and Continuous Hydrothermal Crystallization of Metal
237 Oxide Particles in Supercritical Water, *J American Ceramic Society*. 75 (1992) 1019–1022.
238 <https://doi.org/10.1111/j.1151-2916.1992.tb04179.x>.
- 239 [19] F. Demoisson, R. Piolet, F. Bernard, Hydrothermal Synthesis of ZnO Crystals from Zn(OH)₂
240 Metastable Phases at Room to Supercritical Conditions, *Crystal Growth & Design*. 14 (2014)
241 5388–5396. <https://doi.org/10.1021/cg500407r>.
- 242 [20] C. Pighini, D. Aymes, N. Millot, L. Saviot*, Low-frequency Raman characterization of
243 size-controlled anatase TiO₂ nanopowders prepared by continuous hydrothermal syntheses,
244 *Journal of Nanoparticle Research*. 9 (2007) 309–315.
245 <https://doi.org/10.1007/s11051-005-9061-6>.
- 246 [21] G. Philippot, E.D. Boejesen, C. Elissalde, M. Maglione, C. Aymonier, B.B. Iversen, Insights into
247 BaTi_{1-y}Zr_yO₃ (0 ≤ y ≤ 1) Synthesis under Supercritical Fluid Conditions, *Chemistry of*
248 *Materials*. 28 (2016) 3394–3400. <https://doi.org/DOI:10.1021/acs.chemmater.6b00635>.
- 249 [22] F. Demoisson, Influence of the pH on the ZnO nanoparticle growth in supercritical water:
250 Experimental and simulation approaches, *Journal of Supercritical Fluids*. 95 (2014) 75–83.
251 <https://doi.org/10.1016/j.supflu.2014.08.007>.

- 252 [23] Y. Zhu, G. Seong, T. Noguchi, A. Yoko, T. Tomai, S. Takami, T. Adschiri, Highly Cr-Substituted
253 CeO₂ Nanoparticles Synthesized Using a Non-equilibrium Supercritical Hydrothermal
254 Process: High Oxygen Storage Capacity Materials Designed for a Low-Temperature Bitumen
255 Upgrading Process, *ACS Appl. Energy Mater.* 3 (2020) 4305–4319.
256 <https://doi.org/10.1021/acsaem.0c00026>.
- 257 [24] A. Yoko, G. Seong, T. Tomai, T. Adschiri, Continuous Flow Synthesis of Nanoparticles Using
258 Supercritical Water: Process Design, Surface Control, and Nanohybrid Materials, *KONA*. 37
259 (2020) 28–41. <https://doi.org/10.14356/kona.2020002>.
- 260 [25] A. Aimable, B. Xin, N. Millot, D. Aymes, Continuous hydrothermal synthesis of nanometric
261 BaZrO₃ in supercritical water, *Journal of Solid State Chemistry*. 181 (2008) 183–189.
262 <https://doi.org/10.1016/j.jssc.2007.11.015>.
- 263 [26] A. Yoko, M. Akizuki, Y. Oshima, Formation mechanism of barium zirconate nanoparticles
264 under supercritical hydrothermal synthesis, *Journal of Nanoparticle Research*. 16 (2014).
265 <https://doi.org/10.1007/s11051-014-2330-5>.
- 266 [27] A. Yoko, M. Akizuki, N. Hirao, S. Kohara, M. Kumar, N. Umezawa, T. Ohno, Y. Oshima, In situ
267 X-ray diffraction for millisecond-order dynamics of BaZrO₃ nanoparticle formation in
268 supercritical water, *The Journal of Supercritical Fluids*. 107 (2016) 746–752.
269 <https://doi.org/10.1016/j.supflu.2015.08.002>.
- 270 [28] F. Demoisson, M. Ariane, A. Leybros, H. Muhr, F. Bernard, Design of a reactor operating in
271 supercritical water conditions using CFD simulations. Examples of synthesized
272 nanomaterials, *The Journal of Supercritical Fluids*. 58 (2011) 371–377.
273 <https://doi.org/10.1016/j.supflu.2011.07.001>.
- 274 [29] D. Han, N. Hatada, T. Uda, Chemical Expansion of Yttrium-Doped Barium Zirconate and
275 Correlation with Proton Concentration and Conductivity, *J. Am. Ceram. Soc.* 99 (2016) 3745–
276 3753. <https://doi.org/10.1111/jace.14377>.
- 277 [30] E. Fabbri, D. Pergolesi, S. Licoccia, E. Traversa, Does the increase in Y-dopant concentration
278 improve the proton conductivity of BaZr_{1-x}Y_xO_{3-δ} fuel cell electrolytes?, *Solid State Ionics*.
279 181 (2010) 1043–1051. <https://doi.org/doi:10.1016/j.ssi.2010.06.007>.
- 280 [31] W. Sun, M. Liu, W. Liu, Chemically Stable Yttrium and Tin Co-Doped Barium Zirconate
281 Electrolyte for Next Generation High Performance Proton-Conducting Solid Oxide Fuel Cells,
282 *Adv. Energy Mater.* 3 (2013) 1041–1050. <https://doi.org/10.1002/aenm.201201062>.
- 283 [32] G. Nuñez, M.J. Balanay, R.B.M. Cervera, Preparation of Y-Doped BaZrO₃ Proton Conducting
284 Solid Electrolyte via Modified Low Temperature Pechini Method, *AMR*. 1098 (2015) 86–91.
285 <https://doi.org/10.4028/www.scientific.net/AMR.1098.86>.
- 286 [33] R. Sažinas, C. Bernuy-López, M.-A. Einarsrud, T. Grande, Effect of CO₂ Exposure on the
287 Chemical Stability and Mechanical Properties of BaZrO₃-Ceramics, *J. Am. Ceram. Soc.* 99
288 (2016) 3685–3695. <https://doi.org/10.1111/jace.14395>.
- 289 [34] A.R. Akbarzadeh, I. Kornev, C. Malibert, L. Bellaiche, J.M. Kiat, Combined theoretical and
290 experimental study of the low-temperature properties of BaZrO₃, *Phys. Rev. B*. 72 (2005)
291 205104. <https://doi.org/10.1103/PhysRevB.72.205104>.
- 292 [35] M.F. Hoedl, E. Makagon, I. Lubomirsky, R. Merkle, E.A. Kotomin, J. Maier, Impact of point
293 defects on the elastic properties of BaZrO₃: Comprehensive insight from experiments and ab

- 294 initio calculations, *Acta Materialia*. 160 (2018) 247–256.
295 <https://doi.org/10.1016/j.actamat.2018.08.042>.
- 296 [36] S.B.C. Duval, P. Holtappels, U.F. Vogt, U. Stimming, T. Graule, Characterisation of BaZr_{0.9}Y_{0.1}O
297 _{3-δ} Prepared by Three Different Synthesis Methods: Study of the Sinterability and the
298 Conductivity, *Fuel Cells*. 9 (2009) 613–621. <https://doi.org/10.1002/fuce.200800170>.
- 299 [37] T. Schober, Water vapor solubility and electrochemical characterization of the high
300 temperature proton conductor BaZr_{0.9}Y_{0.1}O_{2.95}, *Solid State Ionics*. 127 (2000) 351–360.
301 [https://doi.org/10.1016/S0167-2738\(99\)00283-0](https://doi.org/10.1016/S0167-2738(99)00283-0).
- 302 [38] Tsvetkov, Ivanov, Malyshkin, Sereda, Zuev, Thermoelectric Behavior of BaZr_{0.9}Y_{0.1}O_{3-d}
303 Proton Conducting Electrolyte, *Membranes*. 9 (2019) 120.
304 <https://doi.org/10.3390/membranes9090120>.
- 305 [39] Y. Yamazaki, R. Hernandez-Sanchez, S.M. Haile, High Total Proton Conductivity in
306 Large-Grained Yttrium-Doped Barium Zirconate, *Chem. Mater.* 21 (2009) 2755–2762.
307 <https://doi.org/10.1021/cm900208w>.
- 308 [40] I. Arvanitidis, D. Sichen, S. Seetharaman, A Study of the Thermal Decomposition of BaCO₃,
309 *Metallurgical and Materials Transactions B*. 27B (1996) 409–416.
- 310 [41] Y. Yamazaki, R. Hernandez-Sanchez, S.M. Haile, Cation non-stoichiometry in yttrium-doped
311 barium zirconate: phase behavior, microstructure, and proton conductivity, *Journal of*
312 *Materials Chemistry*. 20 (2010) 8158–8166. [https://doi.org/DOI: 10.1039/c0jm02013c](https://doi.org/DOI:10.1039/c0jm02013c).
- 313 [42] A. Magrez, T. Schober, Preparation, sintering, and water incorporation of proton conducting
314 Ba_{0.99}Zr_{0.8}Y_{0.2}O_{3-δ}: comparison between three different synthesis techniques, *Solid State*
315 *Ionics*. 175 (2004) 585–588. <https://doi.org/doi:10.1016/j.ssi.2004.03.045>.
- 316 [43] T. Sato, S. Imaeda, K. Sato, Thermal transformation of yttrium hydroxides to yttrium oxides,
317 *Thermochimica Acta*. 133 (1988) 79–85. [https://doi.org/10.1016/0040-6031\(88\)87140-5](https://doi.org/10.1016/0040-6031(88)87140-5).
- 318 [44] F. Demoisson, R. Piolet, F. Bernard, Hydrothermal growth of ZnO nanostructures in
319 supercritical domain: Effect of the metal salt concentration (Zn(NO₃)₂) in alkali medium
320 (KOH), *The Journal of Supercritical Fluids*. 97 (2015) 268–274.
321 <https://doi.org/10.1016/j.supflu.2014.12.012>.

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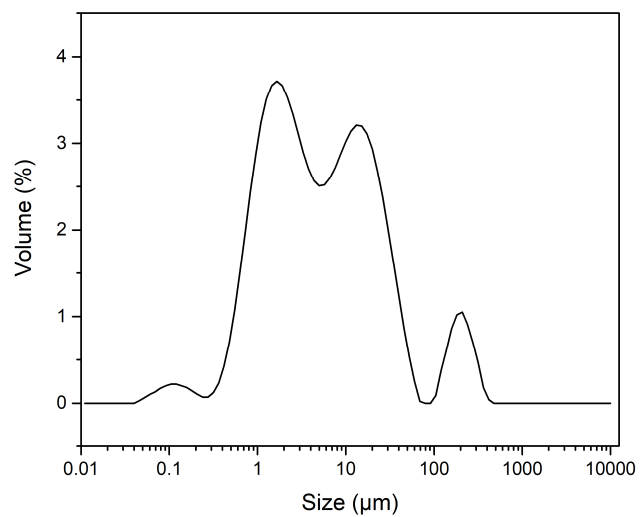
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Figure 1. Schematic of the continuous hydrothermal set-up (adapted from [44]) (Not colored

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for the print version)



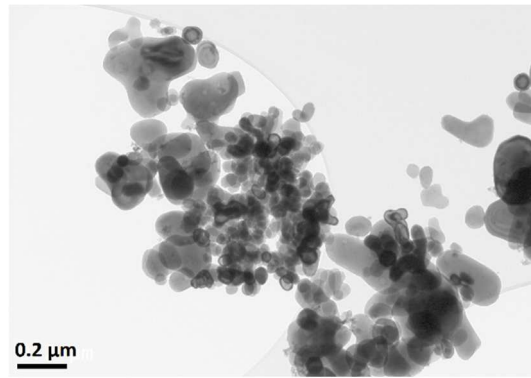
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Figure 2. Particle size distribution by volume of the powder synthesized by the continuous hydrothermal process



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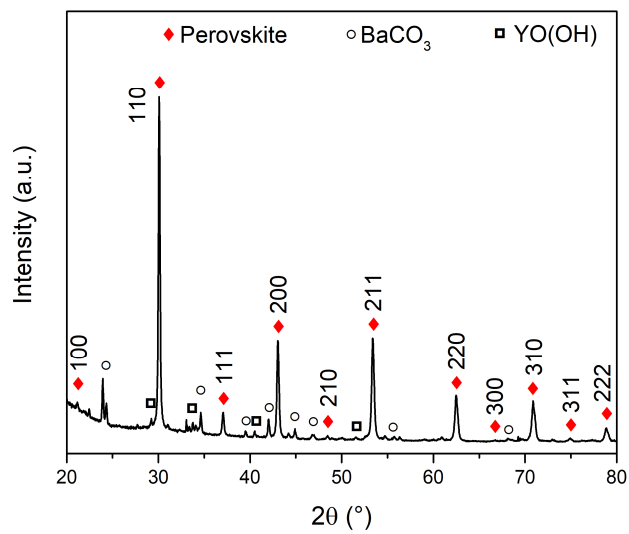
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Figure 3. TEM micrograph of the BZY powder synthesized by continuous hydrothermal process

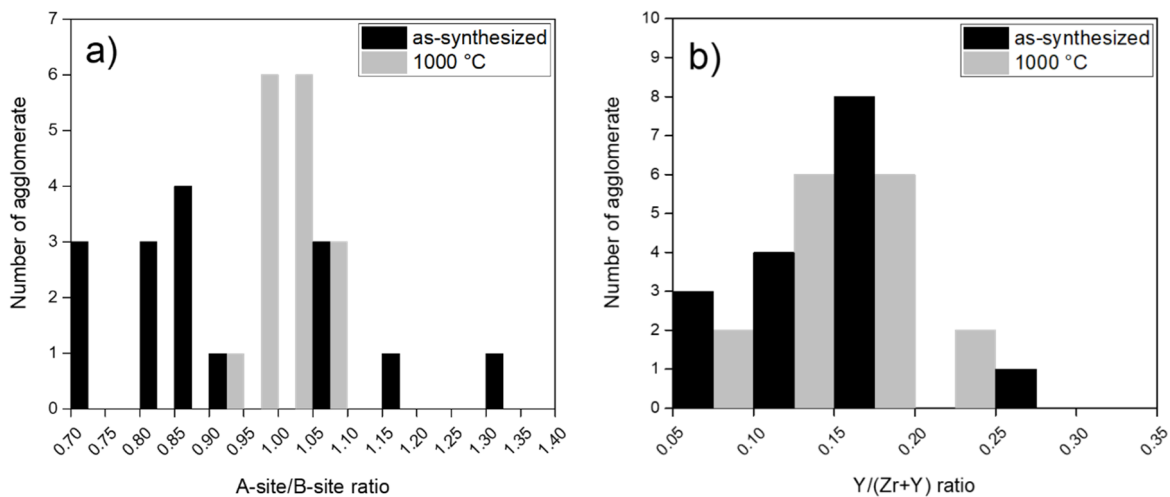
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336 **Figure 4.** X-ray diffractogram of the BZY powder synthesized by continuous hydrothermal
337 process (*Not colored for the print version*)

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Figure 5. a) A-site/B-site ratios and b) Y/(Zr+Y) ratios obtained from EDX measurement on the as-synthesized powder and on the powder annealed at 1000 °C and the corresponding number

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of agglomerates per interval.

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