J. Am. Ceram. Soc., **93** [6] 1572–1575 (2010)
DOI: 10.1111/j.1551-2916.2010.03609.x

Journal

Yttrium-Doped Barium Zirconate Powders Synthesized by the Gel-Casting Method

Dongyun Gao and Ruisong Guo†

Key Laboratory of Advanced Ceramics and Machining Technology of Ministry of Education,
Tianjin University, Tianjin 300072, China

$BaZr_{0.9}Y_{0.1}O_{2.95}$ powders were synthesized using both gel-casting process and solid-state reaction. The gel-casting process with citric acid as the complexing agent could result in nanoparticles with a single perovskite phase. Lower calcining temperature and shorter holding time were required to synthesize the $BaZr_{0.9}Y_{0.1}O_{2.95}$ powders than the traditional solid-state reaction method. The work demonstrates that the gel-casting process is a simple, fast, and convenient method for preparing a high-temperature proton conductor $BaZr_{0.9}Y_{0.1}O_{2.95}$ powder.

I. Introduction

The Y-doped $BaZrO_3$ (BZY) ceramic is one of the most promising proton-conducting materials for solid oxide fuel cell applications. It has desirable properties such as high protonic conductivity and excellent chemical and mechanical stability.[1] However, the refractory nature of $BaZrO_3$-based ceramics results in small grain sizes and high total grain-boundary area. Consequently, this produces an overall low conductivity.[2]

Many efforts are made to densify the $BaZrO_3$-based ceramics. The most common method is to elevate the sintering temperature and prolong the holding time. $BaZr_{0.9}Y_{0.1}O_{2.95}$ samples of 97% theoretical density can be obtained at 1715°C and a holding time of 30 h.[3] Different kinds of sintering aids were tried to lower the sintering temperature of $BaZrO_3$-based ceramics. Among them, ZnO is the most effective one, which can enhance both densification and uniform grain growth. This results in high densities (>93%) at reduced sintering temperature (1300°C).[4,5]

Wet chemical route, such as sol–gel, coprecipitation, combustion synthesis, are also used to synthesize doped-$BaZrO_3$ precursor powder.[6–9] These methods can produce a homogeneous precursor powder at a lower temperature than the traditional solid-state reaction.

Gel-casting is widely known as an attractive ceramic-forming process for making high-quality, complex-shaped ceramic parts.[10] This method can also be used to synthesize multicomponent oxide powder of ceramics and glasses. French scientist Andre Douy first described this process in 1989 and applied the method to synthesize several kinds of powders such as $CaAl_{12}O_9$, $La_{0.8}Sr_{0.2}MnO_3$, $BaZrO_3$, and $CaAl_2Si_2O_8$.[11,12]

The powder gel-casting process combines the advantages of the strong chelation ability of citric acid (CA) in aqueous solution with the steric entrapment effect of an organic polymer. Stable solutions of citrates are easily and rapidly gelled by *in situ* formation of an auxiliary three-dimensional organic network by polyacrylamide. Without a separate drying step, direct pyrolysis yields very fine and highly dispersed powders of mixed oxides and solid solutions.[12]

In this study, both powder gel-casting process and solid-state reaction were applied to synthesize the high-temperature proton conductor $BaZr_{0.9}Y_{0.1}O_{2.95}$. A comparison of the two techniques is presented.

II. Experimental Procedure

(1) Materials

$Ba(NO_3)_2$, $Y(NO_3)_3 \cdot 6H_2O$, $Zr(NO_3)_2 \cdot 5H_2O$, CA, acrylamide, *N*,*N*′-methylenebisacrylamide, and α,α′-azoisobutyronitrile were purchased from Kewei Company (Tianjin, China). All the materials had a purity of 99.9%.

(2) Sample Preparation

(A) Gel-Casting Method: $Ba(NO_3)_2$, $Y(NO_3)_3 \cdot 6H_2O$, and $Zr(NO_3)_2 \cdot 5H_2O$ were weighted in a stoichiometric ratio. These compounds were then dissolved in deionized water separately. The solutions were heated to approximately 60°C to accelerate the dissolving. Then, the three kinds of solution were mixed together and CA was added to the solution in a ratio of CA to nitrate of a 2:1. Ammonia was added to adjust the pH value to 7–8. A premix solution was prepared by dissolving 8 g of acrylamide and 0.8 g of *N*,*N*′-methylenebisacrylamide in 100 mL of distilled water. This premix solution was added to the above nitrate solution under stirring at 2:5 premix solution to nitrate ratio. A few milligrams of the initiator, α,α′-azoisobutyronitrile, were added to initiate the polymerization. The solution with all the ingredients was heated in a dryer to 80°C. About 30 min later, the solution became a translucent gel. The gel was dried at 120°C for 24 h and then calcined at 800°C for 3 h to eliminate the organic ingredients. The amorphous powder obtained was calcined at 1200°C for 4 h to synthesize $BaZr_{0.9}Y_{0.1}O_{2.95}$ powder. The flow chart of this process is shown in Fig. 1.

$BaZr_{0.9}Y_{0.1}O_{2.95}$ powders were also prepared using the same procedure illustrated in Fig. 1 without the steps inside the dash-dotted frame. No CA was used to see if cations can still be fixed *in situ* homogenously in the polyacrylamide network formed by acrylamide, methylenebisacrylamide, and azoisobutyronitrile.

(B) Solid-State Reaction Method: The procedure for the preparation of $BaZr_{0.9}Y_{0.1}O_{2.95}$ powders by the traditional solid-state reaction is mixing $BaCO_3$, ZrO_2, and Y_2O_3 in a stoichiometric ratio and milling the powders in deionized water for 12 h. After drying, the powders were calcined at 1400°C for 10 h in air atmosphere to synthesize the $BaZr_{0.9}Y_{0.1}O_{2.95}$ phase.

In this paper, three kinds of BZY powders are prepared: gel-cast BZY powder with CA, gel-cast powder without CA, and BZY powder synthesized by the traditional solid-state reaction. They are referred as gel-cast BZY–CA, gel-cast BZY, and SSR BZY, respectively.

T. Gur—contributing editor

Manuscript No. 26289. Received June 2, 2009; approved December 16, 2009

This work was financially supported by the National Natural Science Foundation of China under grant No. 50872090.

[†] Author to whom correspondence should be addressed. e-mail: rsguo@tju.edu.cn

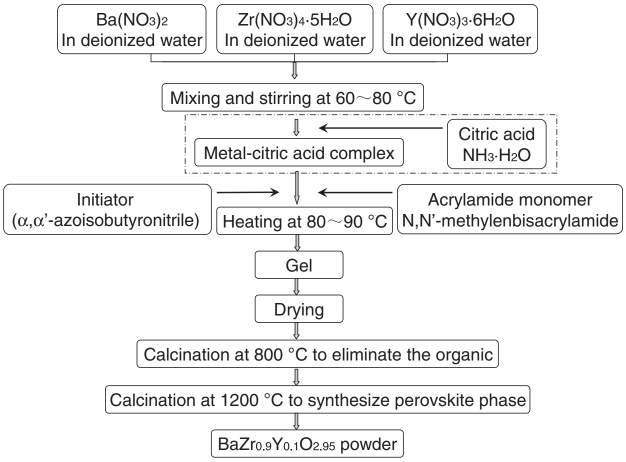


Fig. 1. Flow chart of $BaZr_{0.9}Y_{0.1}O_{2.95}$ powders synthesized by the gel-casting method.

(3) Sample Characterization

Thermogravimetry (TG) and differential scanning calorimetry (DSC) of the dried gel were performed using a NETZSCH STA 449C (Netzsch-Gerätebau GmbH, Selb, Germany) simultaneous TG–DSC analyzer. Samples were heated at 10°C/min from ambient temperature to 1300°C. Powder X-ray diffraction (XRD) data were obtained using a Rigaku D/max 2500 V/PC automatic powder diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu*K*α radiation. Intensities were obtained in the 2θ range between 20° and 90° with a step size of 0.02° and a measuring time of 3 s at each step. XRD data were analyzed using Jade 5.0 software. The grain size and morphology of gel-cast powders and SSR BZY powders were characterized using JEM-1400 transmission electronic microscopy (TEM) (JEOL Ltd., Tokyo, Japan). The specific area was measured at 77 K by NOVA 2000 Series Specific Area Analyzer of Quantachrome Instruments (Quantachrome Instruments, Boynton Beach, FL), with N_2 as the adsorbate gas. Samples were degassed at 200°C for 4 h. The specific surface areas were calculated using the BET multipoint method with five data points. A crystallite size of the 1200°C-calcined gel-cast BZY–CA powders was determined by the X-ray line broadening and calculated using the Scherrer equation:

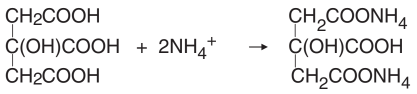
$$D = \frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

where D is crystallite size in nanometers, λ the radiation wave length (0.15405 nm for Cu*K*α), β the corrected full width at half maximum, and θ is the diffraction angle.

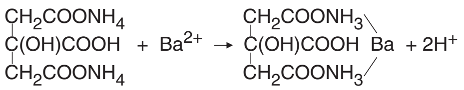
III. Results and Discussion

(1) Gelation Process

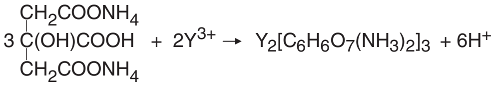
The solution of $Ba(NO_3)_2$, $Y(NO_3)_3 \cdot 6H_2O$, and $Zr(NO_3)_2 \cdot 5H_2O$ forms a complex with CA as the chelating agent in the first step of the gel-casting process. The chemical reactions are as follows:



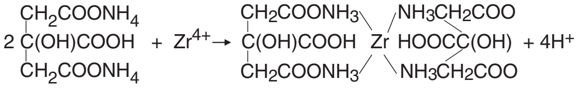
$$\begin{array}{l}CH_2COOH\\ C(OH)COOH\\ CH_2COOH\end{array} + 2NH_4^{+} \rightarrow \begin{array}{l}CH_2COONH_4\\ C(OH)COOH\\ CH_2COONH_4\end{array} + 2H^{+} \qquad (2)$$



$$\begin{array}{l}CH_2COONH_4\\ C(OH)COOH\\ CH_2COONH_4\end{array} + Ba^{2+} \rightarrow \begin{array}{l}CH_2COONH_3\diagdown\\ C(OH)COOH\ \ Ba\\ CH_2COONH_3\diagup\end{array} + 2H^{+} \qquad (3)$$



$$3\begin{array}{l}CH_2COONH_4\\ C(OH)COOH\\ CH_2COONH_4\end{array} + 2Y^{3+} \rightarrow Y_2[C_6H_6O_7(NH_3)_2]_3 + 6H^{+} \qquad (4)$$



$$2\begin{array}{l}CH_2COONH_4\\ C(OH)COOH\\ CH_2COONH_4\end{array} + Zr^{4+} \rightarrow \begin{array}{l}CH_2COONH_3\diagdown\ \ \diagup NH_3CH_2COO\\ C(OH)COOH\ \ Zr\ \ HOOCC(OH)\\ CH_2COONH_3\diagup\ \ \diagdown NH_3CH_2COO\end{array} + 4H^{+} \qquad (5)$$

With the addition of an initiator (α,α′-azoisobutyronitrile) to the solution, the chain-building monomers (acrylamide) form long chains with the cross-linking monomers (*N*,*N*′-methylenebisacrylamide). A very high-molecular-weight polymer, which fills the space and traps the solvent molecules into its branches, is formed. The macroscopic result is a polymer–solvent gel. The gelation time is about 1 h under 80°–90°C. The gel system is pure organic and no foreign ions are introduced to contaminate the solution.

In the gel-casting process, an increased homogeneity of the product is expected because the mixing of the reagents occurs at a molecular level in the solution.

Douy[12] had found that the stability of the complexes is much higher if the pH is raised to neutrality (pH 6–8). Many complexes between CA and metal ions (La, Pb, Bi, …) are insoluble in acidic media but by adding a solution of ammonia as a base, a stable clear solution is obtained rapidly.[12] This complies with our experiments in the synthesis of $BaZr_{0.9}Yb_{0.1}O_{2.95}$ powders. The complex of CA and Yb^{3+} precipitated at a low pH value (acidic), but the precipitation gradually disappeared by adding drops of $NH_3 \cdot H_2O$ solution adjust the pH to neutrality. Although precipitation did not emerge in the acidic solution of

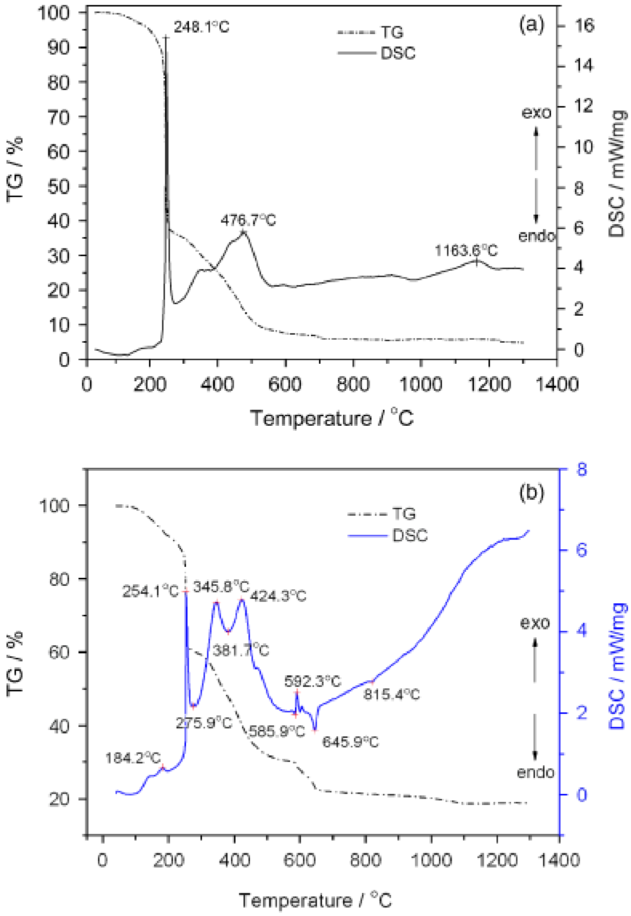


Fig. 2. Thermogravimetry (TG)–differential scanning calorimetry (DSC) curves of BZY gel (a) complexed with citric acid, (b) without citric acid.

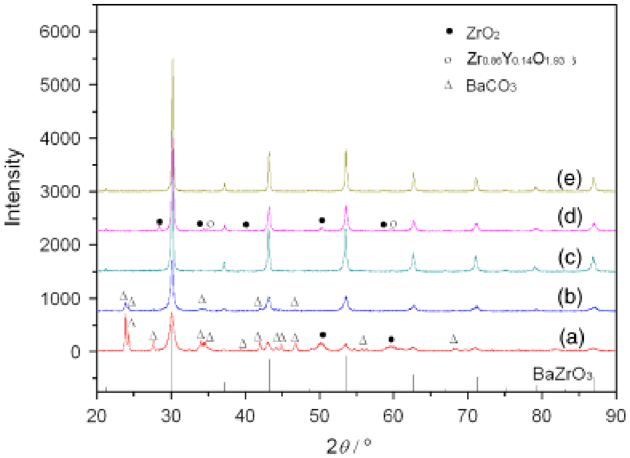


Fig. 3. X-ray diffraction patterns of BZY powders synthesized by the gel-cast and SSR method: (a) gel-cast BZY after elimination of organics at 800°C, (b) gel-cast BZY–CA after elimination of organics at 800°C, (c) SSR BZY calcined at 1400°C for 10 h, (d) gel-cast BZY calcined at 1200°C for 4 h, and (e) gel-cast BZY–CA calcined at 1200°C for 4 h.

$BaZr_{0.9}Y_{0.1}O_{2.95}$, ammonia was still added in order to maintain the consistency with our serial experiments of different dopants.

(2) TG–DSC Analyses

The TG–DSC thermograms of BZY gel complexed with CA and without CA are shown in Figs. 2(a) and (b), respectively.

In Fig. 2(a), the sharp exothermic peak of gel-cast BZY–CA at 248.1°C is due to the reaction between the nitrates and CA, acrylamide, *N*,*N*′-methylenebisacrylamide, and α,α′-azoisobutyronitrile. This reaction releases abundant CO_2 and H_2O, which corresponds to the sharp weight loss in the TG curve. The exothermic peak at 476.7°C is caused by the oxidization of the residue carbon from the combustion of the foregoing reaction. Less heat is released after 600°C, unlike the gel-cast BZY, the heat releasing of which lasts to the end of the testing temperature of 1300°C. The small exothermal peak at 1163.6°C is caused by the phase transformation of monoclinic to tetrahedral ZrO_2. Almost no weight change of the sample is observed after 800°C. The total weight loss of 95.27% is attributed to the elimination of all the water and organics in the gel.

In Fig. 2(b), a sharp exothermic peak appears at 254.1°C. The exothermic peaks of 345.8, 424.3, and 592.3°C are attributed to the burning off of acrylamide, *N*,*N*′-methylenebisacrylamide, and α,α′-azoisobutyronitrile. The weak endothermic peak of 815°C is probably caused by the $\gamma \leftrightarrow \beta$ phase transition of $BaCO_3$. The weight change after 900°C is negligible, but the exothermal effect lasted until the end point of the test at 1300°C. This is perhaps induced by the amorphous phase transforming to a crystal phase. The overall weight loss is 81.28% in the testing temperature range, less than that of the gel-cast BZY–CA, which is 95.27%. Apart from the lack of a chelating agent, the combustion process in gel-cast BZY is not as intense as in the gel-cast BZY–CA, because of the less amount of fuel, thus rendering the weight loss of gel-cast BZY to be less than gel-cast BZY–CA.

Based on the DSC–TG curves, the temperature of eliminating the organics is fixed at 800°C with 3 h of holding time, and that of synthesizing the perovskite phase is set at 1200°C with 4 h of holding time.

(3) Powder Process and Calcination

The elimination of the organics in the gel at 800°C is a thermally induced redox reaction between the oxidizer and the fuel. Based on the principles of the propellant chemistry, the metallic nitrates are used as oxidizers as well as metal element sources. CA, acrylamide, *N*,*N*′-methylenebisacrylamide, and α,α′-azoisobutyronitrile act as fuels apart from their chelating and gelating effects in the solution. All the fuels are the sources of C and H, which form CO_2 and H_2O and liberate heat when burned. Based on the amount of each reactant used, the chemical reaction is proposed as follows:

$$\begin{aligned}&Ba(NO_3)_2 + 0.9Zr(NO_3)_2 \cdot 5H_2O + 0.1Y(NO_3)_3 \cdot 6H_2O\\&+ 2C_6H_8O_7 \cdot H_2O + 4NH_4OH + 2.4H_2C = CHCONH_2\\&+ 0.1H_2C = (CHCONH)_2CH_2 + 17.1O_2 \rightarrow BaZr_{0.9}Y_{0.1}O_{3-\delta}\\&+ 19.8CO_2 + 31.6H_2O + 5.35N_2 \qquad (6)\end{aligned}$$

The actual reaction may not be exactly as proposed because N_2 may be NO, NO_2, or other forms. In addition, the amount of NH_4OH used to adjust the pH may fluctuate slightly every time. α,α′-Azoisobutyronitrile was not considered in the equation due to its small quantity.

After this redox reaction, the organics were eliminated from the gel, and several phases were detected in the powder, as indicated in Figs. 3(a) and (b).

The gel-cast BZY–CA powders were mainly a mixture of $BaZrO_3$ and $BaCO_3$, and the gel-cast BZY powders were a mixture of $BaZrO_3$, $BaCO_3$, and ZrO_2. $BaCO_3$ is formed by Ba^{2+} reacting with the CO_2 gas produced in the redox reaction.

After the elimination of organics, the powders were calcined at 1200°C for 4 h to yield a well-crystallized BZY powder. Figures 3(c)–(e) show the XRD patterns of the powders synthesized by the gel-casting method at 1200°C/4 h and SSR at 1400°C/10 h. It can be seen from the figure that gel-cast BZY–CA powder forms a single perovskite phase, while two other phases, ZrO_2 and $Zr_{0.86}Y_{0.14}O_{1.93}$, are detectable in the gel-cast BZY powder. This indicates that without CA as a chelating agent, the distribution of cations is inhomogeneous in the gel network formed by acrylamide, *N*,*N*′-methylenebisacrylamide, and α,α′-azoisobutyronitrile. This is consistent with the phenomena in the experiment: there is always some water separating out several minutes after the initial gelation of the gel-cast BZY solution, and the pH value of the water is 1–2. This implies that some nitrates are not steadily fixed in the gel by the organic network, even though most of them are immobile in the gel. A single perovskite phase is formed in the SSR BZY powder too, although this is achieved with a much higher calcining temperature and a longer holding time than the gel-casting method.

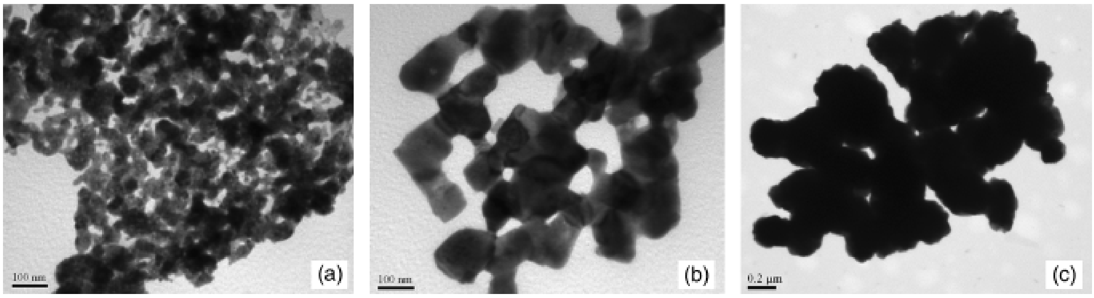


Fig. 4. TEM photographs of gel-cast and SSR powders after calcination at (a) 800°C, (b) 1200°C, and (c) SSR BZY powders calcined at 1400°C.

The XRD patterns in Fig. 3 suggest that the gel-casting method can reduce the synthetic temperature. It is clear that lower calcining temperature is one of the advantages of the powder's liquid solution preparation technology over solid-state reaction.

In all the three samples, the peaks shift to the lower 2θ, which could be explained by the ion size difference between $Y^{3+}(R^{VIII} = 0.1159$ nm) and $Zr^{4+}(R^{VIII} = 0.098$ nm).[13] The cell parameter *a* of gel-cast BZY–CA, calculated using a cubic system and a *P*23 space group (JCPDS 74-1299), was 0.41984 nm, which was slightly larger than that of the pure $BaZrO_3$ phase (0.41815 nm).

Figure 4 shows the TEM photographs of gel-cast powders complexed with CA after calcination at 800° and 1200°C. The TEM photograph of SSR BZY was presented in the same figure for comparison. The powders after the elimination of organics at 800°C are foam-like and fluffy flakes formed by small crystallites. The 1200°C-calcined powders are still puffy, with a grain size of ~50 nm, calculated from the (110) XRD diffraction peak. The crystallite size of SSR BZY calcined at 1400°C was >100 nm, determined with the same method. Not only bigger particle size but also there is agglomeration in the SSR BZY powders. The specific area of gel-cast BZY–CA calcined at 1200°C was 7.53 m^2/g. The grain size of $BaZrO_3$ powders synthesized by Sin *et al.*[6] using the same gel-casting method was ~35 nm. CA combustion process could obtain $BaZrO_3$ powders of ~30 nm.[9] Glycine nitrate combustion synthesis process could synthesize $BaZr_{0.9}Y_{0.1}O_{2.95}$ powders with a specific surface area of ~8 m^2/g.[4] All the results are in the same order with the ones in this paper.

IV. Conclusions

The present work demonstrates that the gel-casting process is a simple, fast, and convenient method to produce high-temperature proton conductor $BaZr_{0.9}Y_{0.1}O_{2.95}$ powder. As the mixing of the constituents in the gel formation is achieved at a molecular level, the powders have a high degree of chemical homogeneity. For gel-cast powders, 1200°C/4 h is enough for the synthesis of a single perovskite phase, while 1400°C/10 h is suitable for the SSR powders.

References

[1] K. D. Kreuer, "Proton-Conducting Oxides," *Ann. Rev. Mater. Res.*, **33**, 333–59 (2003).

[2] P. Babilo, T. Uda, and S. M. Haile, "Processing of Yttrium-Doped Barium Zirconate for High Proton Conductivity," *J. Mater. Res.*, **22**, 1322–30 (2007).

[3] H. G. Bohn and T. Schober, "Electrical Conductivity of the High-Temperature Proton Conductor $BaZr_{0.9}Y_{0.1}O_{2.95}$," *J. Am. Ceram. Soc.*, **83** [4] 768–72 (2000).

[4] P. Babilo and S. M. Haile, "Enhanced Sintering of Yttrium-Doped Barium Zirconate by Addition of ZnO," *J. Am. Ceram. Soc.*, **88** [9] 2362–8 (2005).

[5] S. Tao and J. T. S. Irvine, "A Stable, Easily Sintered Proton-Conducting Oxide Electrolyte for Moderate-Temperature Fuel Cells and Electrolyzers," *Adv. Mater.*, **18**, 1581–4 (2006).

[6] A. Sin, B. El Montaser, P. Odier, and F. Weiss, "Synthesis and Sintering of Large Batches of Barium Zirconate Nanopowders," *J. Am. Ceram. Soc.*, **85** [8] 1928–32 (2002).

[7] A. Magrez and T. Schober, "Preparation, Sintering and Water Incorporation of Proton Conducting $Ba_{0.99}Zr_{0.8}Y_{0.2}O_{3-\delta}$: Comparison Between Three Different Synthesis Techniques," *Solid State Ionics*, **175**, 585–8 (2004).

[8] R. B. Cervera, Y. Oyama, and S. Yamaguchi, "Low Temperature Synthesis of Nanocrystalline Proton Conducting $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ by Sol–Gel Method," *Solid State Ionics*, **178**, 569–74 (2007).

[9] H. P. Kumar, C. Vijayakumar, C. N. George, S. Solomon, R. Jose, J. K. Thomas, and J. Koshy, "Characterization and Sintering of $BaZrO_3$ Nanoparticles Synthesized through a Single-Step Combustion Process," *J. Alloys Compd.*, **458**, 528–31 (2008).

[10] O. O. Omatete, M. A. Janney, and R. A. Strehlow, "Gelcasting—A New Ceramic Forming Process," *Am. Ceram. Soc. Bull.*, **70**, 1641–3 (1991).

[11] A. Douy and P. Odier, "The Polyacrylamide Gel: A Novel Route to Ceramic and Glassy Oxide Powders," *Mater. Res. Bull.*, **24**, 1119–26 (1989).

[12] A. Douy, "Polyacrylamide Gel: An Efficient Tool for Easy Synthesis of Multicomponent Oxide Precursors of Ceramics and Glasses," *Int. J. Inorg. Mater.*, **3**, 699–707 (2001).

[13] R. D. Shannon, "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides," *Acta Crystallogr.*, **A32**, 751–67 (1976). □