Preparation and proton conductivity of ultrafine Y-doped BaZrO₃ ceramics

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Y-doped BaZrO₃ powders prepared by high-temperature solid state reactions often suffer the disadvantage of serious aggregation. In order to eliminate this disadvantage, planet-mill and sand-mill processing methods were employed. The results of particle-size determination and scanning electron microscopy images confirm that sand milling can efficiently eliminate the aggregation and produce ultrafine and well-dispersed Y-doped BaZrO₃ powders. Starting from powders treated by sand milling, completely densified Y-doped BaZrO₃ ceramics can be fabricated by sintering at a low temperature of 1640°C for 15 h. Y-doped BaZrO₃ ceramics sintered from powders treated by sand-mill for 5 h possess an ultrafine crystal size and a higher density and proton conductivity compared to those treated for 2 h.

Key-words : Sand mill, Proton conductivity, Ultrafine ceramics, Y-doped BaZrO₃, Aggregation

1. Introduction

Perovskite-type oxides, such as doped BaCeO₃, SrCeO₃ and BaZrO₃, have attracted the attention of many studies for their role as the solid electrolyte in intermediate temperature Solid Oxide Fuel Cells (SOFCs) due to their excellent proton conductivity in hydrogen or water containing atmospheres.⁰⁻¹¹ Among these, zirconates are favored over cerates for their high chemical stability in H₂O- and CO₂-containing atmospheres and high mechanical strength, increasing their practical application.⁵⁻⁶ Y-doped BaZrO₃ has been demonstrated to be the best candidate for use in SOFCs due to its high proton conductivity, and sufficient chemical and mechanical stability, when compared to other perovskite-type proton conductors.⁴⁻⁷

The application of Y-doped BaZrO₃ as a solid electrolyte in SOFCs, gas sensors and hydrogen pumps requires both high density and high conductivity. However, increasing the density of BaZrO₃-based ceramics remains challenging.⁹ The most widely used synthetic method for their production is via a solid-state reaction, the advantages of which are scalability to mass production, and the simple requirements for equipment and procedures. The main disadvantages of this method are long annealing times, low degree of homogeneity and large particle sizes, resulting in difficulties in the sintering process.⁸⁻¹⁰ Due to its high melting point (~2600°C),¹¹ this method requires very high sintering temperatures (1700–2200°C), with long sintering times on the order of more than 24 h.⁹,¹² This inevitably raises economic costs and results in the evaporation of barium oxide and precipitation of yttria, leading to lower total proton conductivity of the ceramic due to high grain boundary resistance.¹³⁻¹⁵ Such conditions are feasible in laboratory experiments, but are unsuitable in large scale manufacture for practical applications.

Many attempts have been made to improve the sintering. For example, the addition of sintering aids may improve the growth of grain boundaries and result in a decrease in the proton conductivity of doped zirconates.¹⁶⁻¹⁷ Alternative synthesis methods, such as co-precipitation, combustion synthesis, Pechini and sol-gel methods, have been applied to obtain dense BZY at lower sintering temperatures by producing well-dispersed ultrafine powders. However, these fabrication procedures are complicated and suffer from high costs due to expensive precursors and complicated procedures, and are therefore not practical for mass production.¹⁸⁻¹⁹ Moreover, the formation of BaCO₃ as an impurity phase is a common occurrence in doped zirconates prepared by these wet methods, requiring additional calcination steps to remove, resulting in an inhomogeneous composition.²⁰⁻²¹

An effective method to improve the sinter properties is to subject as-synthesized Y-doped BaZrO₃ powder to a second simple ball-milling step in order to create well-dispersed ultrafine particles with fresh surfaces. However, very high temperatures are still required to produce densified ceramics.¹²,²¹ To our knowledge, a systematic study on the role of the degree of dispersion and mean particle size on the sintering process and the resulting proton conductivity of Y-doped BaZrO₃ ceramics prepared by solid-state reaction methods has not been conducted.

In this work, we pulverize powders synthesized by solid-state reaction methods using two mechanical milling techniques: planetary milling and sand milling. The relationships between particle size, sintering and the conductivity of Y-doped BaZrO₃ are investigated.

2. Experimental procedure

BZY10 powder was synthesized using the solid-state reaction method from BaCO₃, ZrO₂ and Y₂O₃ powders (99.9% purity) in stoichiometric amounts. The weighed powder was planetary-ball-milled in ethanol for 24 h and dried at 80°C. The mixed powder was calcined at 1250°C for 4 h in air, resulting in the formation of BaZr₀.₉Y₀.₁O₃₋ₓ

The produced materials were pulverized using two different techniques to eliminate aggregation and obtain small particle sizes and with a uniform size distribution. In the first technique, the powder was planetary-milled for 8 and 24 h separately with
zirconia balls. In the second, a sand-milling method was used with 0.4 mm zirconia beads at 1800 rpm for 1, 2 and 5 h, respectively, in an attritor. The slurry was dried at 80°C. Ethanol was used as the solvent and the ratio of ethanol volume to powder weight was 1:1 in both cases. All samples of dry powders were sieved using a 120 μm mesh and pressed into a pellet, then consolidated by an isostatic press (at 180 MPa) and sintered at 1640°C for 15 h.

The crystal phases of the products were determined by X-ray diffraction (XRD). The particle size distribution of the pulverized slurry was observed using a laser particle analyzer. The morphology and particle size of the powders were observed by scanning electron microscopy (SEM), and micrographs of the cross-sections of sintered compacts were also recorded. The overall proton conductivity was measured by determining the total resistance in H₂O-saturated nitrogen over a temperature range of 300–700°C. The AC impedance measurement was also conducted in H₂O-saturated nitrogen in the frequency range of 20 to 10⁷ Hz at 500°C.

3. Results and discussion

Powders prepared using high temperature solid state reaction methods are usually severely agglomerated. The aggregation of these powders limits the possible extent of densification of the ceramic by sintering. The as-obtained BZY10 powders and treated powders produced by different grinding methods were examined by SEM and are compared in Fig. 1. The SEM images of the as-synthesized powder shows strong agglomeration because of the high annealing temperature [Fig. 1(a)]. After planetary-ball-milling for 24 h, the very large particles are pulverized [Fig. 1(b)] compared to the initial powder, but remain aggregated with unacceptably large sizes, with many particles greater than 3 μm. On the contrary, when the powders were pulverized by sand-milling for 2 h, the particle size was markedly decreased. As seen from Fig. 1(c), the majority of the aggregated powders are totally pulverized into small sized particles, with the exception of some powders that retain some aggregated particles. When milling time was increased to 5 h [Fig. 1(d)], most of the aggregated powders become fully pulverized, with very small sized particles and well-dispersed grains obtained.

The particle size distribution determined by laser particle analyzer can directly reveal the effects of the different milling methods. The average particle size in the as-synthesized powder, planetary-ball-milled powder and sand-milled powder are shown in Table 1. From these data it can be seen that the effects of the planetary mill are limited in reducing the extent of aggregation. However, the particle size in powders that were sand-milled for only one hour were significantly reduced, compared to only very modest reductions in the size when planetary-milled for a whole day, relative to the as-synthesized powders. When sand-milling was performed for as long as 5 h, the mean particle size of the powder was 0.127 μm. These observations are attributed to the differences between the two milling methods, the most prominent of which is the milling speed. As a result, sand milling is more efficient than planetary-milling and provides a superb way to pulverize aggregated powders to produce small sized and well-dispersed particles.

The particle sizes reported by the laser particle analyzer are the aggregated particle size (secondary particle size). Thus, to calculate the crystal size (primary particle size) of different BZY powders, an analysis of the XRD patterns was performed using the Scherrer equation, the results of which are shown in Table 1. It was found that the crystal size of different powders are similar. Therefore, the primary function of the different milling methods is simply to eliminate the aggregation of the powders and not to break the grains.

Using the as-synthesized BYZ powders and the powders treated using the different milling methods, compacts were obtained and compared following sintering at 1640°C for 15 h. Figure 2 shows the XRD patterns of the as-synthesized BYZ powders and the sintered compacts and reveals that the only phase present is Y-

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\begin{array}{|c|c|c|c|}
\hline
\text{Sample} & \text{Milling Time} & \text{Average particle size} & \text{crystallite size} \\
& & (\mu m) & (\text{nm}) \\
\hline
\text{As-synthesized} & & 4.250 & 36.7 \\
\text{Planetary-milled} & 8 h & 2.543 & 37.9 \\
& 24 h & 2.474 & 35.5 \\
\text{Sand-milled} & 1 h & 0.913 & 34.6 \\
& 2 h & 0.441 & 32.7 \\
& 5 h & 0.127 & 31.1 \\
\hline
\end{array}
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![Fig. 1. SEM Micrographs of (a) as-synthesized powders, (b) powders planetary-milled for 24 h, (c) powders sand-milled for 2 h, (d) powders sand-milled for 5 h.](image1)

![Fig. 2. XRD patterns of Y-doped BaZrO₃ of (a) as-synthesize powders; (b) sintered compact from as-synthesize powders; (c) sintered compact from powder planetary-milled for 24 h; (d) sintered compact from powders sand-milled for 2 h; (e) sintered compact from powders sand-milled for 5 h.](image2)
The densities of the sintered pellets from each of the corresponding powders were measured by the Archimedes method using deionized water. These data are summarized in Table 2.

From Table 2, it is clear that the densification of the as-synthesized powders and planetary milled powders at 1640°C is limited due to their high degree of aggregation. On the contrary, high density ceramics can be sintered from sand milled powders at 1640°C for 15 h. Most notably, the sintered compact from the powders that were sand-milled for 5 h achieve almost their full density (99%), which is slightly higher than that prepared by Pechini method (almost 98% sintered at 1800°C for 20 h). These results indicate that sand milling at high rotation speed can efficiently eliminate the aggregation of calcined powders and greatly improve the sintering activity of powders.

The cross-sectional microstructure and morphology of the fractured sintered pellets of un-milled and milled powders were imaged using scanning electron microscopy, as shown in Fig. 3. Figure 3(a) shows that the sintered pellet of the as-synthesized powder has many large pores. Furthermore, the grain size is not uniform due to the wide distribution of particle sizes as well as the presence of many large aggregated particles. The significant degree of porosity and loosely connected grains observed in the SEM images is in agreement with the low relative density of 72%, with significantly high porosity of 26%, as summarized in Table 2. After being planetary-milled for 24 h, similar density, grain size and microstructure were observed [Fig. 3(b)], with slightly improved grain size uniformity and more homogeneous pores. However, the sintering is not substantially improved, with a density of 78% and porosity of 21%, shown in Table 2, consistent with the cross-sectional images. In contrast, sintering is significantly improved when sand-milled for 2 h [Fig. 3(c)]. The cross-section image shows very few pores and a high degree of interconnection between grains, yielding an average size of about 2.5 μm, which is consistent with its high relative density of 97% from Table 2. When increasing sand milling time to 5 h [Fig. 3(d)], the sintered pellet appears to be composed of ultrafine (<1 μm) closely connected grains. The pellet is almost fully densified with ultrafine grains, further confirming the very high relative density of 99% and low porosity of only 0.4%. This microstructure is similar to that prepared by Pechini method which is economically unfavorable for industrial application for expensive precursors and complicated procedures. Consequently, as the particle size of as-synthesized powder diminishes rapidly when pulverized by sand-milling, the sintering is significantly improved leading to highly densified pellets without requiring high sintering temperatures. Typically after sand-milling for 5 h, the aggregated powder is ground into very small and well-dispersed particles (d50~0.127 μm), hence enhancing grain growth and achieving a relative density of 99%, with uniform and ultrafine grains produced by sintering at 1640°C for 15 h. BZY powders prepared by the solid-state reaction method are usually hard to sinter even when using very high temperatures. Thus, sand-milling method provides us with a quite effective way to enhance the sintering performance of the powder.

Figure 4 shows the conductivities of the two powders sand-milled for 2 and 5 h, separately sintered at 1640°C for 15 h, measured under H2O-saturated nitrogen at different temperatures. These data reveal that the conductivity of sintered pellets from the 5 h sand-milled powder is higher than that of the 2 h sample at all selected temperatures. Typically, at 500°C, the conductivity is almost one order of magnitude higher. Previous research indicates that Y-doped BaZrO3 exhibits high bulk conductivity but low total conductivity because of the large grain boundary resistance caused by high sintering temperatures. Thus, many efforts have been made to enhance the grain growth to obtain better grain boundary microstructure and improve the conduction properties. By comparison of the two ceramics from Figs. 3(c) and 3(d), we can clearly see the differences. The ceramics of powders sand-milled for 5 h possess uniform and ultrafine grains with almost no pores, which is beneficial for higher proton conductivity, compared to powders sand-milled for 2 h with a wide distribution and larger size of grains. Thus, obtaining very small and well-dispersed particles by sand-milling significantly improves the conductivity of sintered pellets.
for 5 h greatly improves the sintering performance of BZY and the resulting microstructure of the grain boundaries, sharply reducing the grain boundary resistance. The total proton conductivity of the pellet from the sand-milled powder was measured to reach \(2.14 \times 10^{-3}\) S/cm at 600°C under a H\(_2\)O-saturated nitrogen atmosphere.

The AC impedance spectra of the two samples sand-milled for 2 or 5 h, sintered at 1640°C for 15 h were also obtained under H\(_2\)O-saturated nitrogen at 500°C, as illustrated in Fig. 5. It shows that the resistance of sintered pellet from the 5 h sand-milled powder is much lower than that of the 2 h sample in the low frequency range, which is attributed to grain boundary response. On the contrary, the resistances of the two kinds of samples are similar in the high frequency range, which is due to grain response. This result is consistent with the cross-sectional microstructures and overall conductivities.

### 4. Conclusions

By comparison of as-synthesized, planetary-milled and sand-milled Y-doped BaZrO\(_2\) powders, this work demonstrates that very small size and well-dispersed particles are obtained by sand-milling for 5 h, while no obvious improvements using the planetary-milling method were observed. The sand-milling method eliminates the aggregation of calcined BZY powders, improves their sintering activity and allows a relative density as high as 99% to be obtained, with excellent grain boundary microstructure and uniform, ultrafine grains sintered at a temperature of 1640°C. These factors lead to a higher total proton conductivity. This method has considerable potential for low cost, large-scale production and, most importantly, improved performance of BZY proton conductors. Moreover, this method is expected to be widely applied to turn aggregated powders into ultrafine particles, which are required in many practical applications.

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