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Preparation of Protonic Conductor $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Ln}_{0.2}\text{O}_{3-\delta}$ (Ln=Y, Sm, Gd, Dy) by using a Solid State Reactive Sintering Method

Junfu Bu^{1, a*}, Pär G. Jönsson^{1, b} and Zhe Zhao^{1, 2, c*}

¹Department of Materials Science and Engineering, KTH Royal Institute of Technology, SE-10044 Stockholm, Sweden

²Department of Materials Science and Engineering, Shanghai Institute of Technology, 201418, Shanghai, China

^ajunfu@kth.se, ^bparj@kth.se, ^czhezha@kth.se

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Abstract. Protonic conductors of $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Ln}_{0.2}\text{O}_{3-\delta}$ (BZCLn532, Ln=Y, Sm, Gd, Dy) were successfully synthesized by using a cost-effective solid state reactive sintering (SSRS) method with 1 wt.% NiO as a sintering aid. The pellets of the BZCLn532 were obtained at sintering temperatures between 1300 - 1600 °C. The results show that the morphologies and the final relative densities of the obtained BZCLn532 pellets are influenced significantly when different sintering temperatures were applied. Dense pellets of the BZCLn532 can be obtained at sintering temperatures of 1600 °C for $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Y}_{0.2}\text{O}_{3-\delta}$ and 1400 °C for $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Sm}_{0.2}\text{O}_{3-\delta}$, $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Gd}_{0.2}\text{O}_{3-\delta}$ and $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Dy}_{0.2}\text{O}_{3-\delta}$. The ionic conductivity results show that the $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY532) and $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Dy}_{0.2}\text{O}_{3-\delta}$ (BZCD532) ceramics are demonstrated to be good candidates of oxygen ion conductor and proton conductor materials for intermediate temperature solid oxide fuel cells (IT-SOFCs) applications.

Introduction

Protonic conductor based electrolytes are good candidates for solid oxide fuel cells (SOFCs) applications, due to their promising protonic conductivity at lower operating temperatures. Since Iwahara et al. [1, 2] first reported the proton conduction phenomenon in the ABO_3 perovskite compounds of doped strontium cerates and doped barium cerates, many doped perovskite-type cerates and zirconates compounds have been investigated intensively, especially during the recent years [3-19]. However, high sintering temperatures (normally higher than 1600 °C) and long sintering times (more than 24 h) are always needed for BaCeO_3 - and BaZrO_3 -based ceramic materials to obtain dense bulk materials. But this will lead to very large grain sizes, and eventually result in a low mechanical strength. Thus, this will limit their application for electrolyte-support cell structure designs. Therefore, many wet chemistry methods have been introduced to prepare high quality nanocrystalline powders to decrease the sintering temperatures and sintering times of Barium zirconate and Barium cerate based materials [20]. In addition, various transition metal oxides, such as NiO, CoO, MnO, FeO, ZnO [8, 9, 16-18, 20-26], have been added into the pre-synthesized powder, to improve the sintering behaviour and to achieve a reduced sintering temperature.

Among these alternative methods, the solid state reactive sintering (SSRS) method was improved by Tong et al. [23-25] for $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$, by Coors et al. [26] for $\text{BaZr}_{0.6}\text{Ce}_{0.2}\text{Y}_{0.2}\text{O}_{3-\delta}$ and by Ricote et al. [18] for $\text{BaCe}_x\text{Zr}_{0.9-x}\text{Y}_{0.1}\text{O}_{3-\delta}$ by using NiO as a sintering aid. Therefore, the normal two separate steps solid-state reaction method for synthesize the powder and the sintering of pellets can be combined into one cost-effective single sintering step. Also, as one of the most promising protonic conductor candidates, $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.2}\text{O}_{3-\delta}$ have attracted more and more attention during the recent years [27, 28]. This is due to that it can maintain a good chemical and mechanical stability as well as that it possesses a very good electrical conductivity. Thus, dense ceramic pellets of lanthanides doped barium zirconate-cerate with the formula of $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Ln}_{0.2}\text{O}_{3-\delta}$ (BZCLn532, Ln=Y, Sm, Gd, Dy) were prepared by the solid state reactive sintering method in this study. The obtained pellets were characterized by XRD and SEM. In addition, the relative densities of the BZCLn532 pellets, which were sintered at different sintering temperatures, were also studied.

Experimental

Materials Preparation. BaCO_3 , ZrO_2 , CeO_2 , Y_2O_3 , Sm_2O_3 , Gd_2O_3 , Dy_2O_3 and NiO , powders from Alfa Aesar, were used as starting materials without further treatment in this study. The preparation of a $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY532) compound is taken as an example. Here, stoichiometric amounts of BaCO_3 , ZrO_2 , CeO_2 , Y_2O_3 and 1.0 wt.% of NiO , based on the total weight of BaCO_3 , ZrO_2 , CeO_2 and Y_2O_3 , were weighed. Thereafter, they were milled for 5 h in a water-based milling medium, containing some organic binders. Then, the mixed powder slurry was dried by using a freeze-drier. The compaction of green body was done by using a pressure of 400 MPa for 5 min. Finally, the pellet was sintered for 5 h at temperatures of 1300 - 1600 °C.

Characterization. The pellet morphologies of BZCLn532 were determined by Scanning Electron Microscopy (SEM). Also, phases purity and structures were characterized by XRD, using a Philips X'pert X-ray diffractometer equipped with a graphite monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.540598 \text{ \AA}$). The used step size was $0.0263^\circ \text{ s}^{-1}$ for 2θ values ranging from 20° to 90° . The relative densities of the sintered BZCLn532 pellets were tested in a water medium at room temperature as well as calculated by the Archimedes method.

Result and Discussion

XRD analysis. The XRD patterns of BZCLn532 pellets, which were sintered at a temperature of 1500 °C for 5 h, have been studied. As shown in Fig.1, all of the BZCLn532 compounds were successfully synthesized by the SSRS method. The lattice parameters are refined by the Rietveld method with a Fullprof program. The obtained results show that they have a cubic perovskite structure and belong to the $Pm\bar{3}m$ space group. In addition, it was shown that the peaks of the BZCLn532 system can be indexed as (110), (111), (200), (210), (311), (222) and (321), respectively.

Figure 1 XRD patterns of BZCLn532 pellets prepared at a temperature of 1500 °C and a sintering time of 5 h.

Relative density analysis. Fig. 2 shows the relative densities curve along with the sintering temperatures from 1300 °C to 1600 °C. The relative densities, for a sintering temperature of 1300 °C, were found to be 0.562, 0.773, 0.793 and 0.723 for BZCY532, BZCS532, BZCG532 and BZCD532, respectively. The relative densities of BZCS532, BZCG532 and BZCD532 can be increased to 0.97, 0.96 and 0.98 when a 1400 °C sintering temperature was applied. Furthermore, the relative densities of these three samples were increased to 0.98 (BZCS532 and BZCG532) and 0.99 (BZCD532) when a 1500 °C sintering temperature was applied. However, the relative density of BZCY532 is still lower than that of BZCS532, BZCG532 and BZCD532 for the same experimental parameters, 0.83 (1400 °C) and 0.92 (1500 °C). Fortunately, the relative density of BZCY532 can reach to a value of 0.99 at a sintering temperature of 1600 °C, which is similar to those obtained for BZCS532, BZCG and BZCD532 at 1500 °C. All these results indicate that the Y-substitution at a Ce-site didn't show improved densification behaviour, even with a presence of NiO as a sintering aid. In contrary, with

the addition of a NiO sintering aid, Sm-, Gd- and Dy-substitution at Ce-site can enhance the densification process efficiently. A similar densification behaviour as induced by the Ce-site substitution has been also reported in previous $\text{BaCe}_{0.45}\text{Zr}_{0.45}\text{M}_{0.1}\text{O}_{3-\delta}$ ($\text{M} = \text{In}, \text{Y}, \text{Gd}, \text{Sm}$) research [29].

Figure 2 The influence of the sintering temperatures on final relative densities of the BZCLn532 compounds.

SEM analysis. The sintering temperature is an important controllable parameter in order to obtain dense ceramic materials. Furthermore, the morphology can also change tremendously with a changed relative density. Based on the popular brick-layer model in a SOFC electrolyte analysis, it is crucial to provide a similar relative density and grain size for any comparative study between different electrolyte materials. In view of this, the morphologies of the BZCLn532 compounds, sintered for 5 h at 1300 - 1600 °C, were studied in this research (Fig. 3). The morphologies of all the BZCLn532 pellets are porous when a 1300 °C sintering temperature was used (A1, B1, C1 and D1). It should be noted that the porosity is about 50 vol.% in a BZCY532 pellet at a temperature of 1300 °C, while it is around 30 vol.% for the other pellet types. Some pores still exist inside BZCY532 pellets when they are sintered at a temperature of 1400 °C and 1500 °C (A2-A3). A dense BZCY532 pellet can be only obtained when the sintering temperature reach to 1600 °C (A4). Overall, the porosity decreases with an increased sintering temperature for the BZCY532 compounds. In contrast, when the sintering temperature is increased to 1400 °C, dense pellets of $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Sm}_{0.2}\text{O}_{3-\delta}$ (BZCS532), $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Gd}_{0.2}\text{O}_{3-\delta}$ (BZCG532) and $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Dy}_{0.2}\text{O}_{3-\delta}$ (BZCD532) compounds can be obtained (B2, C2 and D2). A further increase of the sintering temperature up to 1500 °C and 1600 °C, result in almost no open pores inside the pellets of the BZCS532, BZCG532 and BZCD532 (B3-B4, C3-B4 and D3-B4) compounds. However, the resulting grain size is a little too big and the dimensional homogeneity is not so good at a temperature of 1600 °C. Therefore, it is better to sinter the pellets of BZCS532, BZCG532 and BZCD532 at a temperature of 1400 °C or 1500 °C to make the following comparison investigation on ionic conductivity more reliable.

Figure 3 The morphologies of the BZCLn532 pellets after sintered at temperatures of 1300 - 1600 °C and during 5 h.

Conductivity analysis. The conductivities of the BZCY532, BZCS532, BZCG532 and BZCD532 compounds, which were tested in a dry air atmosphere, were found to be $2.5 \times 10^{-2} \text{ S cm}^{-1}$, $4.5 \times 10^{-3} \text{ S cm}^{-1}$, $6.8 \times 10^{-3} \text{ S cm}^{-1}$ and $4.3 \times 10^{-2} \text{ S cm}^{-1}$ at a 600 °C temperature. In contrast, the conductivities of the BZCY532, BZCS532, BZCG532 and BZCD532 compounds, which were tested in a moist air atmosphere, were found to be $2.1 \times 10^{-3} \text{ S cm}^{-1}$, $1.1 \times 10^{-3} \text{ S cm}^{-1}$, $1.5 \times 10^{-3} \text{ S cm}^{-1}$ and $3.2 \times 10^{-3} \text{ S cm}^{-1}$ at a 600 °C temperature [30]. Moreover, the activation energies of the BZCLn532 compounds, which tested in a moist air atmosphere, are always lower than the values that tested in a dry air atmosphere. Thus, it can be concluded that the BZCY532 and BZCD532 compounds are demonstrated to be good candidates for oxygen ion conductor and proton conductor materials for intermediate temperature solid oxide fuel cells (IT-SOFCs) applications.

Conclusions

Fully dense ceramic materials of $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Ln}_{0.2}\text{O}_{3-\delta}$ (BZCLn532, Ln=Y, Sm, Gd, Dy) were successfully synthesized by using a solid state reactive sintering (SSRS) method. 1 wt.% NiO was added as a sintering aid during the sintering process. Based on the obtained morphologies and relative densities data of the BZCLn532 pellets, it is proven that the SSRS method is a good and cost-effective method to prepare the doped barium zirconate-cerate materials. Moreover, NiO was identified that it is an effective sintering aid during the sintering process. Based on the obtained conductivities of BZCLn532 compounds measured in a dry air atmosphere and a moist air atmosphere, $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Y}_{0.2}\text{O}_{3-\delta}$ (ZCY532) and $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Dy}_{0.2}\text{O}_{3-\delta}$ (BZCD532) are good candidates of oxygen ion conductor and proton conductor materials of solid oxide fuel cells operating at intermediate temperatures.

Acknowledgments

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