

Reactive sintering of $\text{BaY}_{0.1}\text{Zr}_{0.9}\text{O}_{3-\delta}$ proton conducting ceramics with CuO liquid phase sintering aid

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The formation of $\text{BaY}_{0.1}\text{Zr}_{0.9}\text{O}_{2.95}$ by solid state reaction and its reactive sintering have been studied. The solid state reaction of a mixture of BaCO_3 , Y_2O_3 and ZrO_2 was studied by differential scanning calorimetry/thermogravimetric analysis and X-ray diffraction. The solid state formation of $\text{BaY}_{0.1}\text{Zr}_{0.9}\text{O}_{2.95}$ is similar to that previously reported for BaZrO_3 . Samples of $\text{BaY}_{0.1}\text{Zr}_{0.9}\text{O}_{2.95}$ were prepared by reactive sintering and the effect of additions of CuO liquid phase sintering aid studied. The densification of reactively-sintered $\text{BaY}_{0.1}\text{Zr}_{0.9}\text{O}_{2.95}$ without CuO addition is very poor. Addition of 4 mol.% CuO causes a 20% increase in density of samples sintered at 1700 °C, as well as promoting grain growth.

Key words: Barium zirconate, proton conductor, solid state reaction, reactive sintering

Introduction

Acceptor-doped BaZrO_3 is a proton conducting ceramic and a leading candidate for use as the electrolyte in proton conducting solid oxide fuel cells [1]. Y-doped BaZrO_3 shows superior conductivity to Y-stabilized ZrO_2 at temperatures lower than 500 °C [2] and good chemical stability in CO_2 and H_2S -containing environments [2, 3]. However, it requires very high sintering temperatures, in the range 1550–1700 °C, and long sintering times, up to 24 h [4, 5]. In order to reduce the sintering temperature and promote densification, various sintering aids such as CuO [6, 7], NiO [8], ZnO [9, 10], Bi_2O_3 and MnCO_3 [11] have been added. Although the addition of sintering aids can improve densification and reduce sintering temperatures, it often causes a decrease in protonic conductivity [10, 11].

As well as conventional sintering, reactive sintering has also been carried out on Y-doped BaZrO_3 [12]. In reactive sintering, the starting materials are mixed together as normal, but are then pressed into pellets and sintered without a prior calcination step. Calcination and sintering take place during sintering of the pellets. A liquid phase sintering aid may also be added to promote densification. Addition of NiO was found to result in a density >95% theoretical density at a sintering temperature of 1400 °C [12].

CuO has been shown to be an effective liquid phase sintering aid for perovskite ceramics [6, 13] but has not yet been used as a sintering aid in reactive sintering of

Y-doped BaZrO_3 . In addition, the calcination process of Y-doped BaZrO_3 has yet to be thoroughly studied. The purpose of this work is therefore to study the calcination process of Y-doped BaZrO_3 and the effect of CuO addition on its reactive sintering.

Experimental

Powders of nominal composition $(100-x)\text{BaY}_{0.1}\text{Zr}_{0.9}\text{O}_{2.95-x}\text{CuO}$ ($x = 0, 2$ and 4 mol.%), hereafter called BYZ, BYZ2Cu and BYZ4Cu, were prepared by ball milling appropriate amounts of barium carbonate (99.8% Alfa Aesar), zirconium dioxide (99.5% Alfa Aesar), yttrium oxide (99.9% Alfa Aesar) and copper oxide (99.7% Alfa Aesar) in a propylene jar in ethanol with ZrO_2 balls for 24 hours. The ethanol was evaporated using a hot plate/magnetic stirrer, followed by crushing of the powder in an agate mortar and pestle and sieving through an 180 μm mesh sieve.

To study the reactions that take place on heating the powders, samples of BYZ powder were analyzed by Differential Scanning Calorimetry/Thermogravimetric Analysis (DSC/TGA, LABSYS evo, Setaram, France). Samples were heated from room temperature to 1250 °C at a heating rate of 10 °C.min⁻¹. Samples of BYZ powder were further heat treated at temperatures in the range 900 °C–1200 °C for 5 hours and then examined by X-ray diffraction (D/MAX Ultima III, Rigaku, Tokyo, Japan) using Cu K α radiation, a scan range of 10–80 degrees 2 θ , a step size of 0.013 ° and a scan speed of 3 °/min.

To sinter samples, 0.5 g of powder was pressed by hand in a 10 mm diameter steel die into pellets. The pressed pellets were then cold-isostatically pressed at 1500 kg/cm² (~147 MPa), placed on a bed of barium zirconate powder (99%, Alfa Aesar) in double high

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purity alumina crucibles with lids and sintered in the temperature range 1500 °C to 1700 °C for 10 hours. The presence of secondary phases in the samples sintered at 1700 °C was determined by X-ray diffraction as before. The microstructures of fracture surfaces of samples sintered at 1700 °C were examined by using a scanning electron microscope (SEM, Hitachi S-4700, Tokyo, Japan). The density of sintered pellets was measured by the bulk method then compared to the theoretical density of BZY10 (6.2 g/cm³).

Results and Discussion

DSC/TGA results of the BYZ powder are shown in Figure 1. The results are very similar to those of Ubaldini *et al.* for the BaCO₃-ZrO₂ system [14] and Duval *et al.* for BaY_{0.1}Zr_{0.9}O_{3-δ} [5]. TGA indicates a small mass loss in the range 730-790 °C, followed by a large mass loss in the range 920-1150 °C. The DSC results show two small endothermic peaks, one with a peak temperature of 820 °C and one with a peak temperature of 980 °C. The two endothermic peaks may correspond to the orthorhombic-hexagonal and hexagonal-cubic phase transitions of BaCO₃ [14]. Both mass losses correspond to a direct reaction between BaCO₃, Y₂O₃ and ZrO₂ to form BYZ [14, 15]

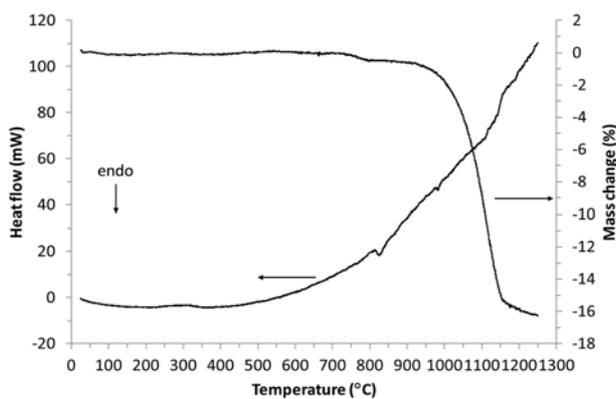


Fig. 1. DSC/TGA analysis of BaCO₃-Y₂O₃-ZrO₂ powder.

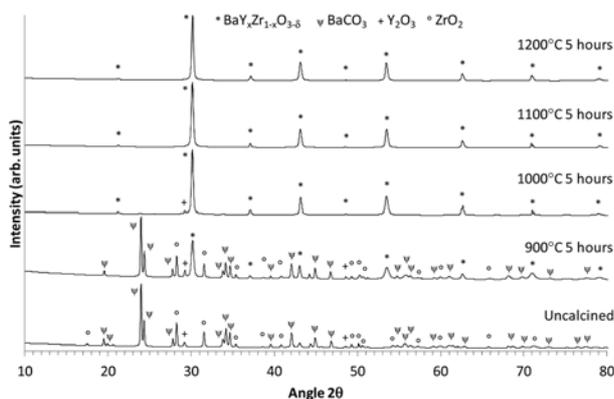
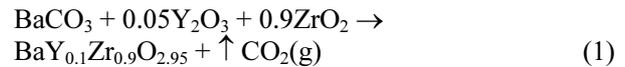


Fig. 2. XRD traces of uncalcined BaCO₃-Y₂O₃-ZrO₂ powder and powders calcined at 900-1200 °C for 5 hours.

as follows:



Unlike the results of Ubaldini *et al.*, DSC peaks corresponding to these weight losses were not observed.

The XRD results for the uncalcined BYZ powder and BYZ powders calcined at different temperatures are shown in Figure 2. The uncalcined powder consists of a mixture of BaCO₃, Y₂O₃ and ZrO₂. The BaCO₃ peaks can be indexed using ICDD card #00-005-0378 for orthorhombic BaCO₃, space group *Pmcn*. The Y₂O₃ peaks can be indexed using ICDD card #90-003-3648 for cubic Y₂O₃, space group *I213*. The ZrO₂ peaks can be indexed using ICDD card #01-086-1451 for monoclinic ZrO₂, space group *P21/c*. After calcination at 900 °C for 5 hours, formation of BaY_{0.1}Zr_{0.9}O_{3-δ} has already started. The formation of BYZ at this temperature corresponds with the first mass loss in the DSC/TGA graph. The peaks for BYZ can be indexed using ICDD card #01-070-3667 for cubic BaZrO₃, space group *Pm3m*. The calcination reaction is almost completed after 5 hours at 1000 °C, with only some unreacted Y₂O₃ remaining. This corresponds to the second mass loss in the DSC/TGA graph. After calcination at 1100 °C for 5 hours, the starting materials are completely converted to single phase BYZ. Rietveld refinement was carried out on the XRD pattern of the BYZ sample sintered at 1100 °C for 5 hours, using the program X'Pert Highscore Plus (PANalytical, Almelo, the Netherlands). The pattern was indexed as cubic, space group *Pm3m* with unit cell parameter *a* = 0.41946(2) nm. *R*_{wp} was equal to 0.01598. This value of unit cell parameter is similar to the results of other workers [5, 12].

The XRD results are similar to those of BaZrO₃ [15]. For BaHf_{0.25}Zr_{0.75}O₃, however, calcination at 1150 ° for 2 hours was not quite sufficient to produce a single-phase powder, with a small amount of BaCO₃ remaining [16]. From the DSC/TGA and XRD results, it is clear that the solid state reaction behaviour of BaZrO₃ and BaY_{0.1}Zr_{0.9}O_{2.95} are very similar. There is a small discrepancy between the DSC/TGA results and the XRD results. The DSC/TGA results show an endothermic peak at 820 °C which was assigned to the orthorhombic-hexagonal phase transition of BaCO₃. However, the XRD results show that only orthorhombic BaCO₃ is present, even after calcination at 900 °C for 5 hours. Ubaldini *et al.* also found similar results [14]. On the contrary, the orthorhombic-hexagonal phase change is seen in the high-temperature XRD of Kozawa *et al.* at 950 °C [15]. The BaCO₃ probably transformed back from hexagonal to orthorhombic during cooling of the samples.

The bulk densities of BYZ, BYZ2Cu and BYZ4Cu samples sintered at 1500-1700 °C for 10 hours are

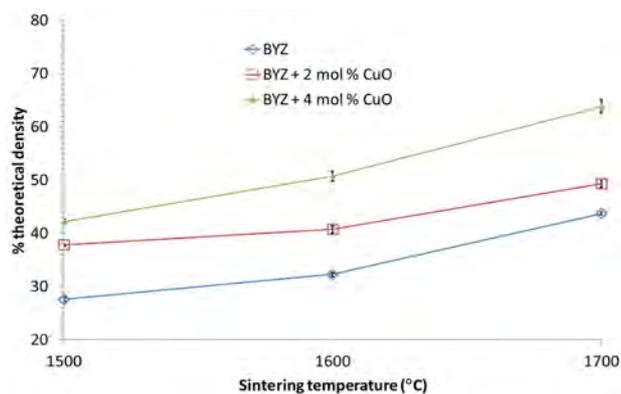


Fig. 3. Bulk density of samples sintered at 1500–1700 °C for 10 hours.

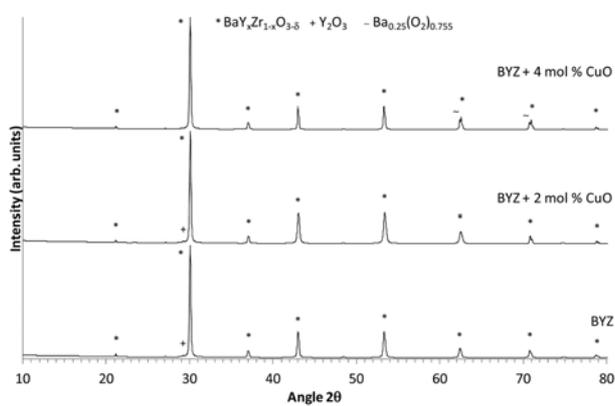


Fig. 4. XRD traces of samples sintered at 1700 °C for 10 hours.

shown in Figure 3. The BYZ powder without addition of CuO shows very poor densification; even after sintering at 1700 °C, the density only reaches 44% of the theoretical density. This behaviour is similar to the work of Tong *et al.*, whose sintering aid-free $\text{BaY}_{0.2}\text{Zr}_{0.8}\text{O}_{3-\delta}$ samples sintered at 1500 °C for 24 hours only obtained a relative density of 35% [12]. Addition of 2 mol.% CuO gives a small improvement, with the sample sintered at 1700 °C reaching a density of 49%. Increasing the amount of CuO to 4 mol.% causes a more considerable increase in density. The density of the sample sintered at 1700 °C is 64% of the theoretical density. However, sample density is still too low to be useful as a solid electrolyte in fuel cells.

XRD traces of samples sintered at 1700 °C for 10 hours are shown in Figure 4. All of the samples contain $\text{BaY}_x\text{Zr}_{1-x}\text{O}_{3-\delta}$ as the major phase. All of the samples contain minor peaks of secondary phases, either Y_2O_3 or $\text{Ba}_{0.25}(\text{O}_2)_{0.755}$ (ICDS card #85-1768). The presence of the secondary phases indicates that BaO volatilization has taken place during sintering [17].

SEM micrographs of fracture surfaces of samples sintered at 1700 °C for 10 hours are shown in Figure 5. The sample without CuO addition [Figure 5 (a)] appears still to be in the initial stage of sintering, with neck formation between particles but few grain boundaries. Grain size is $< 1 \mu\text{m}$ in diameter. Addition

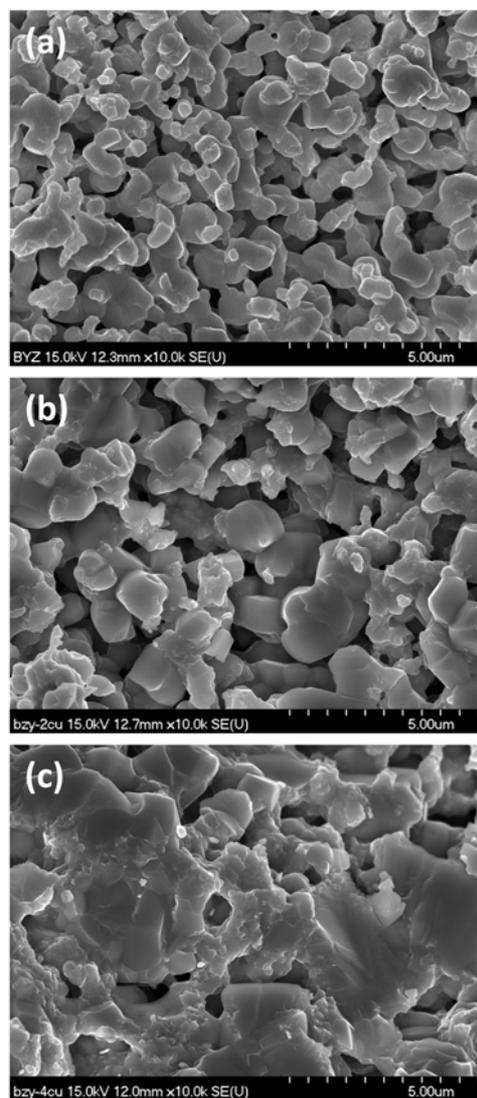


Fig. 5. SEM micrographs of fracture surfaces of (a) BYZ, (b) BYZ2Cu and (c) BYZ4Cu samples sintered at 1700 °C for 10 hours.

of 2 mol.% CuO causes a small increase in density and the grain size increases to 1–2 μm [Figure 5(b)]. Addition of 4 mol.% CuO [Figure 5(c)] causes a considerable increase in both density and grain size. Grain boundaries form between many of the grains and the grain size distribution becomes noticeably broader, with grain sizes varying from less than 0.5 μm to 5 μm . Large intergranular pores are still visible, however.

CuO forms eutectics with BaO at 890 and 900 °C [18] and with ZrO_2 at 1130 °C [19]. The presence of a liquid phase may promote densification by the processes of particle rearrangement, solution-precipitation and pore-filling [20]. The liquid phase may also promote the calcination reaction [equation (1)] by wetting the powder particles and providing pathways for rapid diffusion. A liquid phase that wets the grain boundaries can promote grain growth by increasing the grain boundary mobility [21]. Increased density will also promote grain growth by removing the pore channels

that pin grain boundaries. CuO is known to promote grain growth in BaZrO₃ [7]. In Y-doped BaZrO₃ ceramics, the grain boundary resistance to proton conduction is higher than the bulk, so a reduction in grain boundary area may be beneficial to proton conductivity [9, 12]. The microstructure of the BYZ4Cu sample (areas of high density and grain growth surrounded by large pores) suggests that the CuO sintering aid was not evenly distributed amongst the starting materials. Improved distribution of the sintering aid may further promote densification.

Conclusions

The solid state synthesis of BaY_{0.1}Zr_{0.9}O_{2.95} and its reactive sintering behaviour with additions of 0-4 mol.% CuO have been studied. The solid state synthesis behaviour of BaY_{0.1}Zr_{0.9}O_{2.95} is similar to that of BaZrO₃, with a direct reaction between BaCO₃, Y₂O₃ and ZrO₂ to form BaY_{0.1}Zr_{0.9}O_{2.95}. This reaction has two steps, a minor one beginning at 730 °C followed by the main step beginning at 920 °C. XRD indicated that this reaction was completed after calcination at 1100 °C for 5 hours. The densification of BYZ without addition of CuO was very poor. Addition of 4 mol.% CuO caused a considerable increase in density; however the density is still too low for application as a solid electrolyte. Addition of CuO also promoted grain growth in the sintered samples, which may be beneficial in increasing proton conductivity. Further improvements in densification may be possible by a more homogeneous distribution of the CuO. All of the sintered samples contained secondary phases due to BaO volatilization.

Acknowledgments

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References

1. E. C. Camilo de Souza and R. Muccillo, *Mater. Res.* 13 [3] (2010) 385-394.
2. S. M. Haile, *Acta Mater.* 51 (2003) 5981-6000.
3. J. Li, J. L. Luo, K. T. Chuang and A. R. Sanger, *Electrochimica Acta.* 53 (2008) 3701-3707.
4. S. Imashuku, T. Uda, and Y. Awakura, *Electrochemical and Solid-State Letters.* 10 [10] (2007) B175-B178.
5. S. B. C. Duval, P. Holtappels, U. F. Vogt, U. Stimming and T. Graule, *Fuel Cells.* 9 [5] (2009) 613-621.
6. A. V. Orlov, A. L. Vinokurov, O. A. Shlyakhtin and Y. D. Tretyakow, *Mendeleev Commun.* 14 [4] (2004) 163-165.
7. N. M. Kirby, N. W. Chen-Tan and C. E. Buckley, *J. Eur. Ceram. Soc.* 27 (2007) 2039-2044.
8. S. Ricote and N. Bonanos, *Solid State Ionics.* 181 (2010) 694-700.
9. P. Babilo and S. M. Haile, *J. Am. Ceram. Soc.* 88 [9] (2005) 2362-2368.
10. P. Briois, M. Arab Pour Yazdi, S. Georges, A. L. Shaula, A. Cavaleiro and A. Billard, *ECS Trans.* 25 [2] (2009) 1767-1774.
11. D. Nguyen, Y. H. Kim, G. R. Kim, E. C. Shin, J. S. Lee and J. G. Fisher, "Effect of Bi₂O₃ and MnCO₃ additives on microstructure and electrical properties of BaY_{0.1}Zr_{0.9}O_{2.95} proton conducting ceramics", submitted to *Solid State Ionics*.
12. J. Tong, D. Clark, M. Hoban and R. O' Hayre, *Solid State Ionics.* 181 (2010) 496-503.
13. J. G. Fisher, D. G. Lee, J. H. Oh, H. N. Kim, D. Nguyen, J. H. Kim, J. S. Lee and H. Y. Lee, *J. Kor. Ceram. Soc.* 50 [2] (2013) 157-162.
14. A. Ubaldini, V. Buscaglia, C. Uliana, G. Costa and M. Ferretti, *J. Am. Ceram. Soc.* 86 [1] (2003) 19-25.
15. T. Kozawa, K. Yanagisawa and Y. Suzuki, *J. Ceram. Soc. Jpn.* 121 [3] (2013) 308-312.
16. H. Y. Tian, D. Y. Wang, J. Q. Qi, Y. Wang, H. L. W. Chan and C. L. Choy, *J. Alloys Compounds.* 402 (2005) 251-255.
17. P. Babilo, T. Uda and S. M. Haile, *J. Mater. Res.* 22 [5] (2007) 1322-1330.
18. W. Zhang, K. Osamura and S. Ochiai, *J. Am. Ceram. Soc.* 73 [7] (1990) 1958-64.
19. A. M. M. Gadalla and J. White, *Trans. Br. Ceram. Soc.* 65 (1966) 383-90.
20. R. M. German, P. Suri and S. J. Park, *J. Mater. Sci.* 44 (2009) 1-39.
21. J. D. Powers and A. M. Glaeser, *Interface Science.* 6 (1998) 23-29.