Journal of Engineering and Science Research 1 (2): 79-84, 2017
e-ISSN: 2289-7127

DOI: 10.26666/rmp.jesr.2017.2.14

Effect of Double Heat Temperature Profile on $Ba(Ce,Zr)O_3$ Sintered Pellet

Azliana Ramli[1], Nafisah Osman[1] and Nurul Wahida Othman[2]
[1]Faculty of Applied Sciences, Universiti Teknologi MARA, 02600 Arau, Perlis, Malaysia.
[2]Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.

Abstract: The preparation technique during synthesizing process and heat treatment plays an important role in the properties of the ceramic materials. In this paper, ceramic perovskite-type oxide based on Ba $(Ce,Zr)O_3$ was prepared by sol-gel method and sintered via two-step sintering (TSS) technique. In the TSS, the sintered pellet was undergoing twice heat treatment. The first temperature profile was set at T_1= 1400°C and the second temperature were varied at T_2 = 1150°C, 1200°C, 1300°C and 1350°C, respectively. XRD results showed that all samples TSS1 to TSS5 exhibit single-phase of cerate-zirconate ceramics except for the pellet sintered at 1300°C (TSS4). The crystalline peaks for single-phase sintered pellets were matched to the standard compound $Ba(Ce,Zr)O_3$. On the other hand, the presence of secondary phases of CeO_2, Ba_2ZrO_4 and $BaCO_3$ along with the main phase of $Ba(Ce,Zr)O_3$ were detected in TSS4. SEM analysis revealed that the samples formed clear and compact grains with submicron sizes whereby the size of grain decreased from 336.4 to 192 nm as the second sintering temperature increased. This paper attempts to show that the implementation of different sintering profile in TSS method was found to give significant effect on the phase and morphology of solid solution of $Ba(Ce,Zr)O_3$.

Key words: *Two-step sintering, $Ba(Ce,Zr)O_3$, phase identification, cerate-zirconate ceramics*

INTRODUCTION

Energy demand has led to tremendous research for an alternative to renewable energy conversion technology. Solid oxide fuel cells (SOFCs) is an alternative that offer more efficiency in conversion of chemical energy in fuels into electricity whereby there were embark interest in reduce the operating temperature in range of 500-700°C for long-term stability and cost-effective approach. On the other hand, a proton conducting fuel cells (PCFCs) were under intense study due to lower operating temperature (less than 800°C) compared to the conventional oxygen ion SOFCs [1]. In this paper, low activation energy of cerate-zirconate compound with perovskite structure ABO_3 was one of the promising candidates as solid electrolyte for better proton conduction in PCFCs applications. Better understanding of proton conduction in solid electrolyte of cerate-zirconate required understanding on the role of synthesizing process and heat treatment in controlling the material's structure, phase morphology as well as the de-densification phenomenon that affected by the heat treatment sintering process.

Recent research have found that double heat treatment so-called Two-Step Sintering (TSS). It is the cost-effective sintering method which can be implementing in order to improve the ionic conductivity of ceramic material. This technique was discovered by Chen and Wang for sample Y_2O_3 to obtain full-dense and nano-grain size ceramics [2]. This novel technique has found be able to control the microstructural features of ceramics such as grain size, density and reduce the heating time to hinder the grain growth [3]. However, to obtain high density pellet at relatively low temperature was a challenging process particularly for the electrolyte ceramics based on perovskite-oxide type. So far this TSS method has only been applied done to Y_2O_3, $BaTiO_3$, ZnO, Y-TZP, $MgSi_2$ and Al_2O_3 [2-5], but there was still insufficient data for the $Ba(Ce,Zr)O_3$ ceramics. This paper attempts to show the effect of sintering profile on the sample's structure, phase morphology as well the explanation of de-densification phenomenon after undergo TSS heat treatment.

Corresponding Author: Azliana Ramli, Universiti Teknologi MARA, Faculty of Applied Sciences, Universiti Teknologi MARA, 02600 Arau, Perlis, Malaysia., no.phone

MATERIALS AND METHODS

Powder of $Ba(Ce,Zr)O_3$ via sol-gel method

Starting chemical precursors of $Ba(NO_3)_2$ (99% ACROS), $Ce(NO_3)_3$ (99.5% ACROS), $Zr(NO_3)_2$.xH2O (99.5% ACROS) and $Y(NO_3)_{3.5}$H2O (99.9% Aldrich) were dissolved in deionized water and continuously stirred for 24 hours. Citric acid, ethylene glycol and ethylenediaminetetraacetic acid (EDTA) were added as chelating agent and polymerization agent, respectively [6]. Ammonium hydroxide was added to promote the dissolution of EDTA. The solution was heated and stirred to achieve fully chelated gel. The sol-gel undergo heat treatment at 325°C within 2 hours and kept before calcination. The as-synthesized powder was then calcined at 1100°C in 10 hours to form BCZY powder samples. Finally the powder was grinded in a planetary grind using agate mortar to produce nano-sized $Ba(Ce,Zr)O_3$ powder.

Pellet Preparation

The calcined $Ba(Ce,Zr)O_3$ powder was placed in a steel mold and hydraulic uniaxial compacted in a pellet die under pressure of 369 MPa for 5 minutes. The prepared pellets with the same dimension if 1.2 cm in diameter and 0.1-0.2 cm thickness were then subjected to the sintering study of TSS (labeled as TSS1, TSS2, TSS3, TSS4 and TSS5) and conventional sintering step (CSS) as for comparison analysis.

Sintering Process

In TSS technique, the sintering was carried out using five heating regime routes. The pellets were undergo initial temperature T_1 = 1400°C with heating rate of 5°C/min and held at T_1 for 1 minute, then rapidly cooled down to T_2 (1150°C, 1200°C, 1250°C, 1300°C and 1350°C) with the cooling rate of 30°C/min within 10 hours as tabulated in Table 1.

Table 1: Two-Step Sintering (TSS) Temperature Parameters

Heating regime	T_1 (°C)	t_1 (min)	T_2 (°C)	t_2 (hour)
TSS1	1400	1	1150	10
TSS2	1400	1	1200	10
TSS3	1400	1	1250	10
TSS4	1400	1	1300	10
TSS5	1400	1	1350	10

Characterization

All samples (pellet) were characterized in terms of phase, relative density, morphology and grain size analysis. X-Ray Diffractometer (XRD) (Shimadzu) was used to verified the phase formation of sintered pellet via Cu-Kα radiation (λ =1.5406Å) at 2θ from 20° to 80° in step of 0.02° with scanning time of 2.5 seconds in each step. Meanwhile, the relative density of the sample were determined by analyzed the ratio between the value of density obtained from the geometrical method and theoretical value of 6.11 g cm-3. For grain size analysis, at least 100 grains were examined using image analyzer of Image-J software.

RESULTS AND DISCUSSION

Phase Identification

The crystalline peaks for single-phase perovskite samples were matched to the standard $Ba(Ce,Zr)O_3$ with JPCDs card no 01-089-2485, except for S4. Figure 1 revealed the XRD pattern of BCZY sample after sintered at CSS and various TSS profile. As seen in Figure 1, the additional small peak at 2θ = 44.12° in S3 due to the impurity of $BaCO_3$. Meanwhile, the presence of secondary phases in S4 impurities of CeO_2, $(Ce,Zr)O_2$ and $BaCO_3$ were observed in the XRD pattern. As reported in previous work, at this calcination temperature, the powder still consist remaining carbonate residue [7]. For the pellet sintered at 1300°C, the $BaCO_3$ impurity was decomposed and subsequently impeded a complete formation of BCZY.

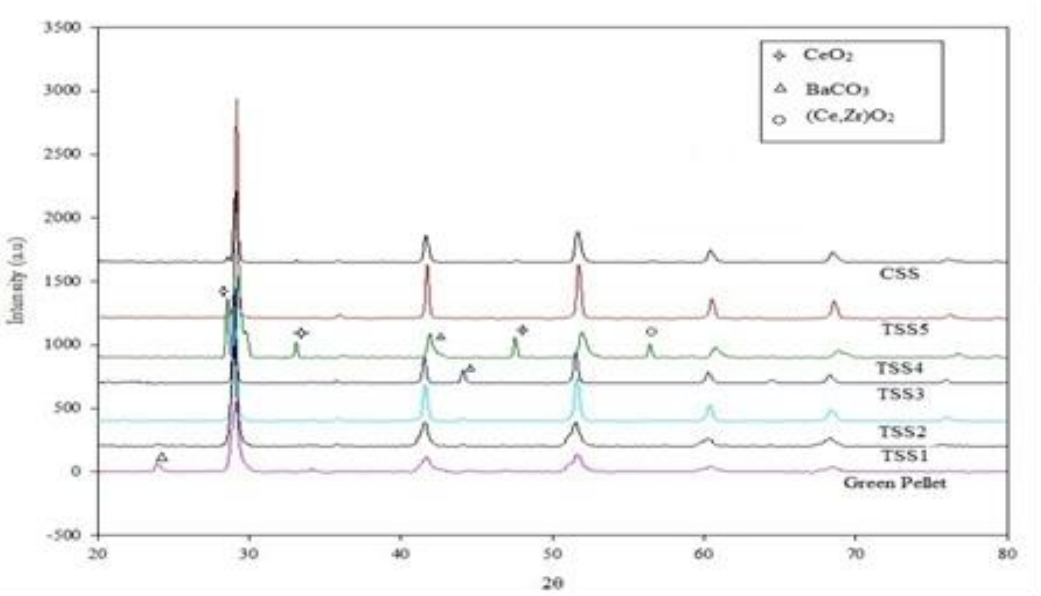

Figure 1: XRD spectra for green pellet, TSS1, TSS2, TSS3, TSS4, TSS5 and CSS

Relative Density

The relative densities of the sintered pellets were increased as the increase in sintering temperature, except for S4 as shown in Figure 2. De-densification phenomenon was occurred as sintering temperature increased up to the decomposition temperature of remaining $BaCO_3$. The same observation was also reported by Shlyakthin for the $La_{0.7}Ca_{0.3}MnO_3$ sample at 1300°C [8]. A simple explanation that attribute to this behavior was related to the chemical nature of the compound components, secondary crystallization or exaggerated grain growth and formation of gasses (O_2, CO_2 and SO_2) due to high temperature decomposition process. Equation 1 express the possible chemical reaction for the decomposition process in TSS4 sample. Pores were formed due to the releasing of CO_2 and consequently decreased the relative density of the pellet.

$$BaCO_3 \rightarrow BaO + CO_2\ (g) \qquad \text{(Eq.1)}$$

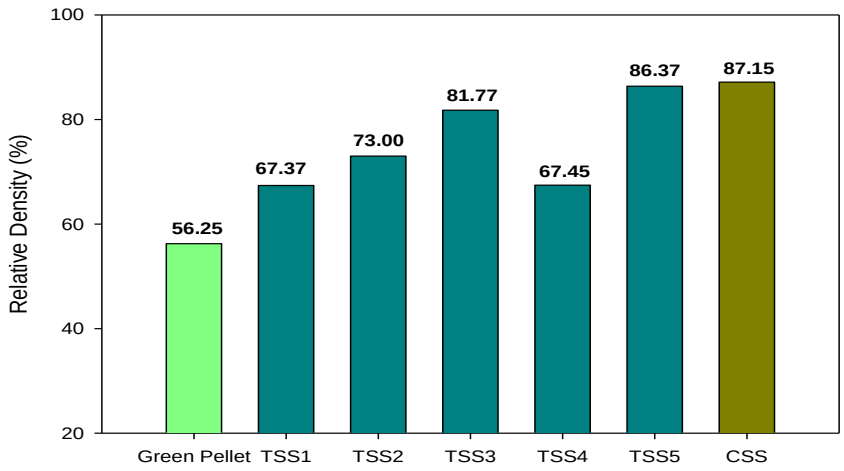

Figure 2: Relative density distribution of BCZY pellets.

Grain Size Analysis

Grain size distributions of all pellets in nanoscale were shown in Figure 3. As calcination temperature increased, the grain sizes of the pellets were also increased. However, as T_2 increased up to 1250°C (TSS4), the grain size of pellets was also increased and then started to reduce during the decomposition of remaining carbonate species as the T_2 reached 1300°C.

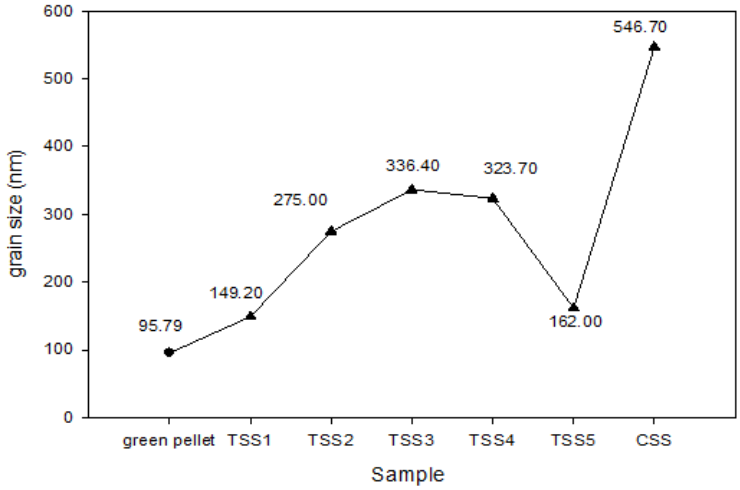

Figure 3: Grain size (nm) distribution of BCZY pellets.

Regard to the density and grain size, TSS5 exhibit highest density with comparable small grain size. The grain size was rapidly decreased and formed dense pellet due to the de-densification phenomena. The reduction of grain size at 1350°C might be due to the deceleration of grain boundary migration and finally reduce the rate of grain growth [9]. However, the grain size of the CSS pellet was much larger than the sintered pellets suing TSS method.

A possible explanation on the increasing in density and decreasing in grain size after de-densification phenomena can be explained based on these two conditions. First, the initial sintering temperature, T_1 does affect the T_2. A 'kinetic window' exists between T_1 and T_2, whereby the diffusion occurs when grain boundary or bulk movement was restricted. Second, the selection of T_2 also contributes to the grain growth. When the T_2 was very high, the grain growth was also increased. In contrast, when the temperature is reduced, densification will diminished due to suppression of atomic diffusion which result incomplete densification, as reported by A. S. A. Chinelatto [10].Density that exceeds a certain critical value will minimize the density of triple junction which leads to the mechanism in controlling the grain growth.

Microstructure for $Ba(Ce,Zr)O_3$ pellets was shown in Figure 4. SEM analysis revealed that the samples formed clear and compact grains with submicron sizes. For the TSS profile, the size of the grain decreased from 336.4 nm to 162.0 nm. The samples exhibited similar morphology with spherical shape. The SEM micrograph conformed the TSS pellets were well-sintered yielded to the homogenize grain size. On the other hand the grain size of sample sintered by CSS method was relatively larger compared to TSS method.

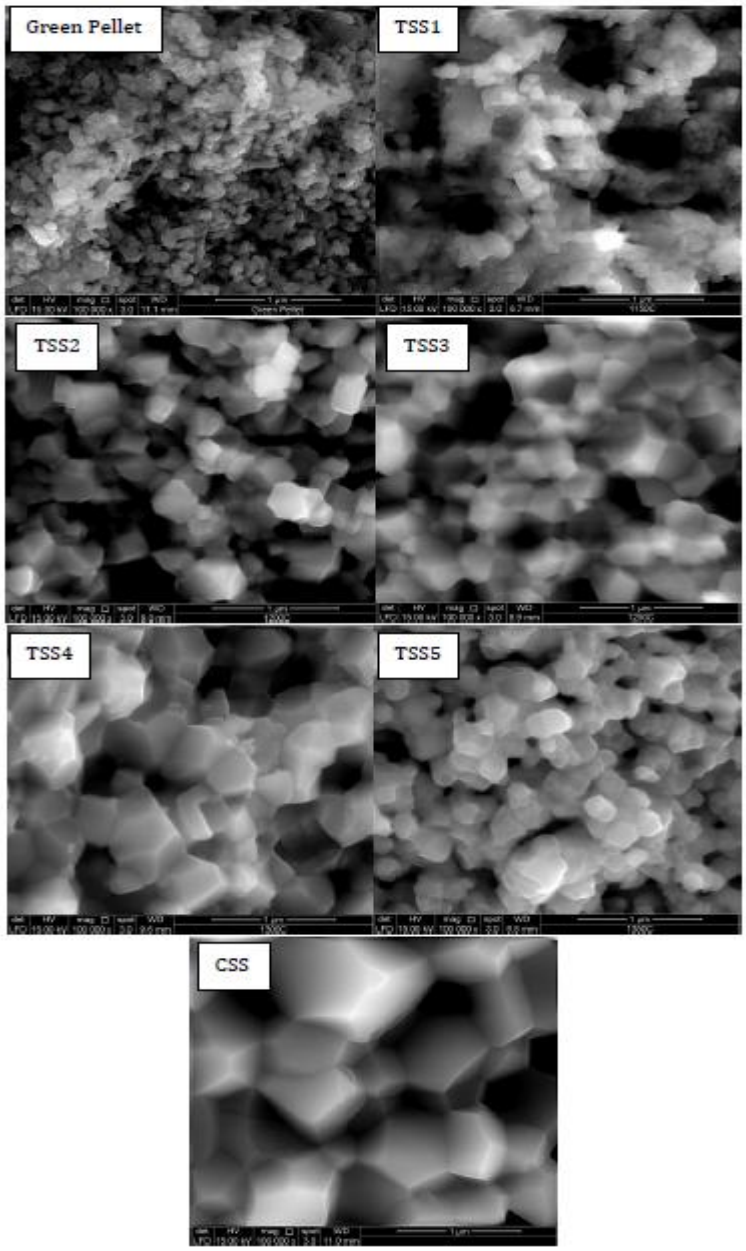

Figure 4: Microstructure of BCZY pellets.

CONCLUSION

The implementation of different sintering heat treatment in TSS method was found to give significant effect on phase formation and morphology of Ba(Ce, Zr)O_3 solid solution. Decomposition of carbonate residue reduced the density of sintered pellets due to the de-densification phenomenon as observed at T_2 = 1300°C. At T_1=1400°C and T_2=1350°C, TSS method has been successfully done to reduce the grain size of high density Ba(Ce,Zr)O_3 pellet at sintering temperature lower than CSS method. Further work on the different TSS profiles is in progress and will be reported elsewhere.

REFERENCES

[1] A. K. Baral, 2015. Reduction in sintering temperature of stable proton conductor $BaCe_{0.35}Zr_{0.5}Y_{0.15}O_{3-\delta}$ prepared by sol-gel method and its transport properties. Solid State Ionics, 272: p. 107-111.

[2] X. H. Wang, X. Y. Deng, H. L. Bai, H. Zhou, W. G. Qu, L. T. Li and I. W. Chen, 2006. Two-step sintering of ceramics with constant grain-size, II: $BaTiO_3$ and Ni-Cu-Zn ferrite. Journal of the American Ceramic Society. 89: p. 438-443.

[3] A. Nadernezhad, F. Moztarzadeh, M. Hafezi and H. Barzegar-Bafrooei, 2014. Two step sintering of a novel calcium magnesium silicate bioceramic: Sintering parameters and mechanical characterization. Journal of the European Ceramic Society. 34: p. 4001-4009.

[4] M. Mazaheri, A. Simchi and F. Golestani-Fard, 2008. Densification and grain growth of nanocrystalline 3Y-TZP during two-step sintering. Journal of the European Ceramic Society. 28: p. 2933-2939.

[5] Z. R. Hesabi, M. Haghighatzadeh, M. Mazaheri, D. Galusek and S. K. Sadrnezhaad, 2009. Suppression of grain growth in sub-micrometer alumina via two-step sintering method. Journal of the European Ceramic Society. 29: p. 1371-1377.

[6] N. Osman, N. A. Abdullah and S. Hasan, 2014. Chelating agent role in synthesizing cerate-zirconate powder by a sol-gel method. Advanced Materials Research. 896: p. 1-7.

[7] N. A. Abdullah, S. Hasan and N. Osman, 2013. Role of CA-EDTA on the synthesizing process of cerate-zirconate ceramics electrolyte. Journal of Chemistry. p. 1-7.

[8] O. A. Shlyakthin, Y. J. Oh and Y. D. Tretyakov, 2000. Preparation of dense $La_{0.7}Ca_{0.3}MnO_3$ ceramic from freeze-dried precursors. Journal of European Ceramic Society. 20: p. 2047-2054.

[9] M. M. Billah, A. Mousharraf and M. F. Islam, 2011. The effect of sintering time on the densification of pure nano-sized $BaTiO_3$. International Conference on Mechanical Engineering 2011 (ICME2011): p. 1-4.

[10] A. S. A. Chinelatto, A. L. Chinelatto, C. L. Ojaimi, J. A. Ferreira and E. M. A. Pallone, 2014. Effect of sintering curves on the microstructure of alumina-zirconia nanocomposites. Ceramic International. 40: p. 14669-14676.