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Characterisation of microstructure and hardness of perovskite-structured $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ under different sintering conditions

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Abstract

Microstructural evolution of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) has been investigated using commercial powders sintered at different conditions. All the samples, characterised by the porosity P and grain size D , are determined to be a single cubic phase. The grain growth kinetics is evaluated using $D^n = tK_0 \exp(-Q/RT)$. Grain boundary diffusion is the dominant controlling mechanism of densification and the Ba/Sr diffusion is the rate-controlling species. Additionally, the Vickers hardness (H_V) of BSCF is measured at ambient condition. The H_V is successfully described by an exponential function of porosity, $H_V = H_0 \exp(-bP)$. The porosity is the dominant factor determining the hardness when it is over 0.06. Otherwise, the Vickers hardness shows a dependence on pore size. Compared with the strong dependence of hardness

on porosity, no correlation between hardness and grain size or grain orientation has been found.

Keywords: Porosity; Hardness; BSCF; Grain growth kinetics; EBSD

1 Introduction

Currently, mixed ion-electron conducting(MIEC) materials have been attracting great attention due to their high oxygen permeation which makes them not only promising oxygen separation membranes, but also candidate materials used as solid oxide fuel cells[1]. Among these MIEC materials, perovskite-structured $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) membranes have been of great interest due to their 100% selective permeation in theory and high-efficiency properties at elevated temperature during the operation process[2].

It has been known that microstructural features, such as grain boundary structure and grain size, have an influence on functional and mechanical properties of ceramic materials[3-5]. On the other hand, the microstructure depends on the history of processing, and particularly on the sintering procedures, even for similar compositions. Since it has been reported that the permeation properties of BSCF ceramic membranes are directly dependent on their microstructure [6, 7], it is necessary to investigate the microstructural development of these membranes.

Although oxygen stoichiometry[8], oxygen permeation properties[9] and the aspects of chemical stability of BSCF[10] have been widely investigated, less work about

mechanical properties of BSCF has been carried out, especially the effect of microstructure (grain size, pore size) on the hardness [11, 12] to the best of our knowledge. Generally, hardness, an important parameter, is associated with a number of important properties or performance aspects of ceramics [13]. For example, the hardness is an essential prerequisite of evaluating the fracture toughness of ceramic materials [14]. The utility of hardness is further enhanced by the fact that it is obtained by a simple indentation test that can be rapidly performed on relatively small samples at moderate cost [15].

The hardness of ceramics is typically a function of both grain size and porosity. As for some ceramic materials, grain orientation [16] and chemical decomposition [17] also affect hardness. From the literature, the dependence of hardness on grain size does not always show a single trend that applies to every ceramic material [15], as suggested by Rice *et al.* who have reviewed the relationship between grain size and hardness of a variety of oxides and non-oxide ceramics [15]. For example, studies on ceramic materials including MgO, BeO, Al₂O₃, MgAl₂O₄ and B₄C[15] as well as hydroxyapatite [18] have shown that an increase in grain size leads to a decrease in hardness. In contrast, the hardness of some other ceramic materials such as TiB₂, SiC, TiC and Si₃N₄ is essentially independent of grain size[15]. According to Shaffer's research on silicon carbide [16], crystallographic orientations also have an effect on hardness determined by Knoop method.

In this work, the microstructural evolution of a BSCF material with different sintering

temperatures and periods of dwell time is studied and the effect of microstructure on hardness is then investigated. The aim of this work is to investigate the sintering mechanisms of the BSCF material and provide more systematically understanding of the correlation between hardness and microstructure of the BSCF material.

2 Experimental procedure

2.1 Sample preparation

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ powder used in this study was supplied by Treibacher Industrie AG, Austria. The powder was packed in a cylindrical stainless steel die with a diameter 28 mm, and uniaxially pressed under a pressure of 100MPa. The cold-pressed powder was divided into two groups. The first group was sintered between 900 and 1150°C for 10 hours in air and nine different types of samples were acquired. The second group was sintered at 1100°C for 1, 5, 10, 24, 50 and 100 hours and six different types of samples were obtained. The heating rate and the cooling rate during the process of sintering were set to 180°C/hour. After sintering, the diameters of the samples shrank from 28 mm to approximately 21 mm. The BSCF bars were cut into disc-shape samples with a thickness of 2 mm using a diamond saw in a precision cut-off machine. The samples were then ground using several different sizes of SiC grinding papers from P400 to P1200, and then polished with diamond paste descending from 6 μm to a final stage of 0.25 μm .

2.2 Microstructural and thermal characterisation

The porosities of all the samples were determined by the Archimedes method in distilled water. The wide range of sintering conditions was included in this study in order to produce samples having a wide range of porosities and grain sizes. The phase of all the BSCF samples was analysed using X-ray diffraction (XRD; PW1830, Philip, Eindhoven, the Netherlands) with CuK_α radiation ($\lambda=0.154$ nm). The patterns were refined by TOPAS software (Bruker 4.2). The lorentz polarization factor was fixed to 17. The background was fit by chebychev polynomials of 3th order. The peaks were fit using PV_TCHZ function. The cubic phase was refined using Tomkiewicz *et al.* [19] structure model based on a cubic cell ($Pm-3m$). The refined parameters were zero error, the lattice parameter and crystal size. The parameter of the instrument is fixed as the following values shown in Table 1. The error bars of lattice parameters were calculated from the at-least-square fitting during the refinement. Microstructural evolution under the various sintering conditions was examined using a scanning electron microscope (SEM; Quanta FEG-650, FEI). Grain size and grain orientation were analysed by electron backscatter diffraction (EBSD, NordlysNano, Oxford Instruments). The diameters of the grains were determined by HKL Channel 5 software using $D = \sqrt{\frac{4S}{\pi}}$, where D is grain size and S grain area determined by the software)]. The pore size was quantified by Image-Pro Plus 6.0 software based on SEM images. The agglomerate size distribution of powder was measured by laser light scattering (Mastersizer, MicroTrac X100, Malvern, UK). To evaluate the mass change during sintering, BSCF powder was heated from room temperature to 1150°C

in air in thermogravimetry (TG, SETARAM, K/SETEVO15-1A) during which the mass of the powder was monitored. The measurement of temperature was recorded within an accuracy of 0.001 °C, and the measurement of mass was recorded within an accuracy of 0.02 µg.

2.3 Macro-indentation and Micro-indentation

Hardness measurements were made by indentations on polished faces of the BSCF samples using a diamond indenter (CSM Instruments, Peseux, Switzerland). The tip geometry and machine compliance were calibrated prior to testing. The hardness of the samples was determined according to ISO/FDIS Standard 14577-1[20]. The maximum load of 10 N was applied for macro-indentation test. The procedures of making indentations were followed by a sequence of loading (30 seconds), dwelling at the maximum load (10 seconds) and unloading (30 seconds). Two 10×10 indentation matrixes per sample were made, and the distance between adjacent points was more than 5 times the indentation size ($\sim 200\text{ }\mu\text{m}$). Indentations that ended up with surface chipping were not included in the analysis.

To understand the effect of crystallographic orientation on hardness, some indentions were made on a relatively large area covering grains with different orientations. To minimise effect of pore and grain boundary and maximise the measured grain number, a compromise was reached by selecting a sample sintered at 1100°C for 10 hours for the micro-indentation test. A small load (100 mN) was used in this test in order to minimise the chance of indenting on pores. Four 10×10 indentation matrixes were

carried out. Afterwards, the crystallographic orientations of individual grains with indentation impressions were determined by EBSD. The values of the indentation at surface pores and near grain boundaries were excluded in subsequent analyses. All the values of hardness were calculated by software (Wilson Tukon 2100, Instron, Germany).

3 Results and discussion

3.1 Powder characterisation

Figure 1(A) shows the XRD pattern of the starting BSCF powder. The powder is identified as single cubic perovskite structure and the diffraction peaks correspond to the reflections (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 0), (2 1 1), (2 2 0), (3 0 0), (3 1 0), (3 1 1), and (3 2 1). The XRD analysis is in agreement with the result of previous work [21], which has revealed that no other phases in the starting powder. Thus, it can be inferred that the starting powder is highly crystalline and composed of pure cubic BSCF particles. The particle size distribution of the powder is shown in Figure 1(B), which shows a broad range of particle sizes with a bimodal distribution. The average particle size is determined to be around 3 μm . SEM micrographs of the powder in Figure 1(C) confirm the presence of soft agglomerates and a wide primary particle size distribution.

3.2 X-ray Diffraction

Figure 2(A-B) show the room temperature XRD patterns of the BSCF samples sintered at different conditions in this study with all peaks indexed corresponding to the ICSD card NO.109462[22]. All peaks are indexed as cubic perovskite structure in line with previous reports [23-25]. Even at high temperature up to 1150°C, the BSCF samples do not decompose and no other phase can be found by XRD. This means that BSCF exhibits good phase and structure stability at high temperature in air.

Figure 2(C-D) show the lattice parameters of BSCF sintered at different conditions determined using Rietveld refinement on the basis of the XRD data. The lattice parameter of the starting powder at room temperature was determined as 3.9790Å in this work, which is similar to the value reported by Koster *et al.* (3.9830Å)[26]. As shown in Figure 2(C), the lattice parameter of BSCF increases from 3.9862 to 3.9905 as the dwell time increases from 1 to 10 hour at 1100°C. Subsequently, the lattice parameter shows little change from 10 to 100 hours. For a given sintering time (10 hours) in Figure 2(D), it can be observed that the lattice parameter increases linearly with increasing sintering temperature, which is consistent with the results obtained by Wang *et al.*[27]. Within the temperature range studied, the maximum variation of the lattice parameters of BSCF is 0.32%.

Figure 3 shows the weight change of BSCF sintered between 1000°C and 1150 °C. In the whole temperature range covered (between 1000°C and 1150°C), the weight of BSCF keeps decreasing. Between 1000°C and 1100°C, the weight loss predominantly

occurs during the heating up stage, and when the samples are held at a certain temperature, there is little weight loss. Between 1125°C and 1150°C, the weight loss is higher than that between 1000°C and 1100°C. Also, when the samples are held at 1125°C and 1150°C, the weight loss can be also observed and the weight loss at 1125°C is similar to that at 1150°C. According to the research from other groups [28-31], the weight loss is mainly associated with the loss of lattice oxygen. This can cause the formation of oxygen vacancies and the valence change of transition metal ions. The associated reaction can be written in the Kroger-Vink notation as[32]

where M refers to Fe or Co. The weight losses at 1125°C and 1150°C are heavier, which suggests that the loss of lattice oxygen in this range becomes more active. It has been reported [29-31] that these changes are closely linked with the decrease from high valence state Fe^{4+} and Co^{3+} to low valence state Fe^{2+} and Co^{2+} , with the loss of lattice oxygen, which can be also expressed by

The loss of oxygen results in oxygen vacancies. In order to maintain the charge neutrality, high valence state Fe^{4+} and Co^{3+} are transformed into Fe^{2+} and Co^{2+} and their effective ionic radii are enlarged[33]. According to McIntosh *et al.*[28], the increase in concentration of oxygen vacancies can result in an increase of lattice

parameter. Therefore, the loss of lattice oxygen and the formation of oxygen vacancies can be the reason for the observed increase in lattice parameters with increasing sintering temperature.

3.3 Grain evaluation

For a given sintering temperature of 1100°C, the average grain size grows rapidly as the dwell time increases from 1 to 10 hours, followed by a gradual decrease in the growth rate as the thermal exposure time further increases from 10 to 100 hours, as shown in Figure 4(A).

According to the analysis of grain growth kinetics conducted by Hillert *et al.*[34] and Mendelson *et al.*[35], investigators [36-40] have obtained the following grain growth kinetics at a constant temperature:

$$D^n - D_0^n = tK_0 \exp\left(-\frac{Q}{RT}\right) \quad (4)$$

where D (μm) is average grain size at the time t ; D_0 is the initial average grain size; n is the kinetic grain growth exponent, K_0 is a constant, Q is the apparent activation energy (kJ/mol); R is the gas constant, 8.314 J/mol·K; T is the absolute temperature (K).

Because the average grain size of the samples sintered at 900°C is 1.52 μm , it is reasonable to expect that the original grain size D_0 should be no more than this value.

On the other hand, the value of n is normally in the range from 1 to 4. The grain sizes

of BSCF sintered at 1100 °C are in the range of 14 μm to 35 μm. Therefore, $\frac{D^n - D_0^n}{D^n}$ is approximately 1, and Eq. (4) is simplified as follows:

$$D^n = tK_0 \exp\left(-\frac{Q}{RT}\right) \quad (5)$$

Therefore, n can be determined from the slope (1/n) of $\ln$ (grain size) versus $\ln$ (time) line, as shown in Figure 4(B). At a sintering temperature of 1100°C, the slope 1/n is determined to be 0.33. This means that the value n of grain growth exponent equals 3, which is consistent with that obtained by other groups (n=3.1)[25] and other perovskite-structured materials such as PrBaCo₂O_{5+δ} (n=3) sintered at 1150°C from 6 to 48 hours[40].

Figure 4(C-E) show the microstructures of BSCF sintered at 1100°C for various dwell time. It is noted that the average grain size increases with increasing dwell time. The average grain sizes of the samples sintered at 1100°C from 1 to 100 hours are found to be in a range from 14 μm to 35 μm.

As shown in Figure 5(A), the average grain size grows with an increase in sintering temperature for a given sintering time (10 hours). The grain size increases slowly with increasing sintering temperature up to 1000°C, followed by a faster growth rate in the range from 1000 to 1100°C. Between 1100 and 1150°C, the grain size enters the period of rapid growth. For instance, the average grain size of the BSCF samples sintered at 900, 1050, and 1150°C was determined to be 1.52, 13.4 and 64.8 μm, respectively, with their corresponding microstructures shown in Figure 5(D-F).

Figure 5(B) shows an Arrhenius plot obtained by constructing the data of average grain sizes from a constant dwell time, in which $\ln(D^3/t)$ is plotted versus the reciprocal of the absolute temperature ($1/T$). Assuming that the grain growth exponent ($n=3$) is independent of temperature, it is used to determine the activation energy for BSCF grain growth. The logarithm of the Equation (5) obtains the slope which can be used for calculation of the apparent activation energy for the grain growth. There exists a reasonably good linear relationship between $\ln(D^3/t)$ and $1/T$ from 900 to 1150°C at the constant dwell time (10 hours) in this study ($R^2=0.950$). The grain growth activation energy determined from the slope of Figure 5(B) is 650.7 ± 30 kJ/mol. Although Salehi *et al.*[6], Baumann *et al.*[7] and Yoon *et al.*[41] have not reported activation energies for grain growth of BSCF, analysing their data yields activation energies in the range from 372 to 741 kJ/mol as plotted in Figure 5(C), which fairly agree with the result in this study.

3.4 Mechanisms of densification and grain growth

It is a very difficult undertaking to unambiguously identify the controlling mechanisms taking account of the simultaneous occurrence of densification and coarsening processes. Coble *et al.*[32] have proposed a model to determine the controlling mechanism of densification for the final stage of sintering. This model predicts that the densification rate $\frac{d\rho}{dt}$ is given by the following equation:

$$\frac{d\rho}{dt} = \frac{CN\xi\gamma_s\Omega}{D^m} \quad (6)$$

where ρ represents the density, C denotes a constant, N is the number of pores inside a grain, γ_s refers to the surface energy, Ω denotes volume per cation, D is average grain size to the power m , where m depends on the rate-controlling mechanism for densification, ξ is the relevant diffusion coefficient. For $m=3$ densification is controlled by lattice diffusion or interface reaction, while for $m=4$ grain boundary diffusion controls the densification[42]. Accordingly, the m value can be determined by plotting a log-log of Equation (6) to determine the slope.

The experimental data obtained from the samples sintered at 1100°C from 5 to 100 hours are plotted in this way for the density ranging from 93.7% to 95.5% in Figure 6(A). At 1100°C, the calculated value of m from the plot is 3.98 ± 0.29 for BSCF as shown in Figure 6(B). Considering the values of m , it is suggested that the grain boundary diffusion is the dominant controlling mechanism for BSCF at 1100 °C.

In the case of grain growth kinetics, the grain growth exponent n of BSCF is determined to be 3. In other words, the grain growth kinetics of BSCF materials do not follow the classical parabolic law ($n=2$). A higher grain growth exponent indicates slowly coarsening grains. It has been reported that the driving force for grain growth is the local curvature of the grain boundary[32]. When the pores are dragged along the grain boundary, it will lower the driving force for grain boundary mobility thereby slowing grain growth[14]. A grain growth exponent greater than 2 can be related to pores and impurity contents of the oxide materials [27, 28]. Therefore, it can be observed in Figure 5(D-F) that pores can be the dominant factor for the higher grain

growth exponent.

With regard to the activation energy for grain growth of BSCF, it is calculated to be 650.7 ± 30 kJ/mol. Because the activation energy for oxygen ion diffusion (45-105 kJ/mol[43, 44]) is much lower than this value, it is suggested that cations are the rate-controlling species of grain growth rather than oxygen ions. According to the studies performed by Lein *et al.* [44, 45], the diffusion of Sr/La has been observed to be slower than that of Co/Fe in $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and the activation energy for Sr/La diffusion is 619 KJ/mol. Therefore, it can be speculated that the Ba/Sr diffusion can be the rate-controlling species during the sintering process of BSCF.

3.5 Hardness analysis

The porosities of BSCF samples sintered at 1100°C for different periods of time (from 5 to 100 hours) are very similar (5%) while the average grain size of these samples shows a range of 18.0 to 35.2 μm [Figure 7(A)]. As shown in Figure 7(B), there appears to be a small linear dependency of the Vickers hardness of sintered BSCF samples on the inverse square root of the grain diameter [$1/\sqrt{D}(\mu\text{m}^{-\frac{1}{2}})$]. In view of this poor correlation coefficient and the very small implied linear coefficient [Figure 7(B)], it is suggested that the hardness values of the sintered BSCF samples in this study are probably independent of grain size.

Figure 8(A) shows an EBSD map of the surface area on a BSCF sample sintered at 1100°C for 10 hours where indentations were made. The orientations of the individual

grains are colour coded, with the colour representing the crystallographic orientation parallel to surface normal. The black areas in the image, which are not indexed in the EBSD orientation maps, corresponding to pores and indentations. One matrix of the indentation impressions has been framed with white dotted lines.

As can be seen in Figure 8(B), there is no substantial difference in depths of penetration into the surface and the nearly 80 load-displacement curves are almost overlapped. It is suggested that the hardness shows no clear correlation with the crystallographic orientation. As for BSCF samples, the value of Vickers hardness were chosen from the indentation on pore-free surface area and away from grain boundaries as shown in the Figure 8(A). In this way, it makes pores effect on the Vickers hardness less critical. The average Vickers hardness under the loading 100 mN is 12.1 ± 0.5 GPa. This value is much higher than the average of Vickers hardness under the load of 10 N due to the indentation size effects[46]. And there is only a small deviation (less than 4%) for the obtained values. Therefore, it is suggested that the grain orientations have no obvious influence on Vickers hardness when the porosity is lower than 0.06.

The BSCF samples sintered from 900 to 1150°C for 10 hours were used to investigate the effect of porosity on hardness. The volume fraction porosity is ranged from about 0.05 to 0.27, with the mean grain sizes ranging from 1.52 to 64.8 μm .

Figure 9(A) shows the relative density of BSCF as a function of sintering temperature.

The Vickers hardness of the sintered BSCF strongly depends on sintering temperature, as shown in Figure 9(B). As grain size and grain orientation have been confirmed to

have negligible effect on the hardness, it indicates that the relative density/porosity plays a dominant role in determining the Vickers hardness. According to the Minimum Solid Area (MSA) model proposed by Rice [47, 48], it can be represented by [48]

$$H_V = H_0 \exp(-bP) \quad (7)$$

where H_V is the measured indentation hardness, H_0 is the Vickers hardness value corresponding to a specimen with zero porosity, b is a material dependence constant and P is the volume fraction porosity of the specimen. The hardness-porosity relationship can also be written in a linearised form [$\ln(H_V)$ vs P]. The linear fit to Equation (7) yielded values of 7.05 ± 0.54 GPa for H_0 and 3.40 ± 0.32 for the constant b , with a R^2 value of 0.954 in Figure 9(C). The zero-porosity value of Vickers hardness H_0 , 7.85 ± 0.87 GPa obtained from the literature values [12, 49] by the linear regression analysis surpassed Vickers hardness ($H_0 = 7.05$ GPa) measurements on BSCF samples in this study, because indentation size effects [24, 50] normally exist in Vickers hardness test (1 N loading for the literature and 10 N loading for this study). As shown in Figure 9(B), the Vickers hardness increases with increasing sintering temperature from 900 to 1100°C, because the porosity decreases from 0.27 to 0.05. At the sintering temperatures between 1100 and 1150°C, the total porosities of BSCF samples stay similar and the average grain size increases from 22 to 64.8 µm, but the Vickers hardness decreases gradually. As previously discussed, the grain size and grain orientation show no clear correlation with the values of indentation hardness of

BSCF samples. In other words, the total porosity is the dominant factor to determine the values of Vickers hardness of BSCF samples. But when the total porosity is similar, there can be another factor to affect the values of Vickers hardness of BSCF samples.

The microstructures of the BSCF samples sintered at 1100, 1125, and 1150°C for 10 hours were shown in Figure 10. The average pore size is 1.56, 1.62 and 2.51 μm for the samples sintered at 1100°C, 1125°C, and 1150°C for 10 hours, respectively, determined by the Image-pro Plus 6.0 software. The average pore size increases with increasing the temperature from 1100 to 1150°C, which is attributed to the “Ostwald Ripening” mechanism[51]: vacancies diffuse away from regions of high curvature (small pores) and sink at the relatively large pores which have low surface curvature, causing them to grow. It has been reported that increasing pore size negatively influences mechanical properties[52]. Therefore, it is suggested that the increase in pore size can decrease hardness determined by the macro-indentation methods under the loading of 10N when the total porosity is lower than 0.06.

4 Conclusions

Commercial BSCF powder has been sintered at various conditions. All the BSCF samples show a single cubic perovskite structure. Grain growth process in sintered BSCF has been systematically investigated. The average grain size of the BSCF samples sintered at 1100 °C increases proportionally to the one-third power of sintering time ($n= 3$), with an apparent activation energy of 650.7 ± 30 kJ/mol. Grain

boundary diffusion is the dominant controlling mechanism of densification and the Ba/Sr diffusion is the rate-controlling species during the sintering process of BSCF at 1100°C. There is no clear grain size dependence of hardness determined by the Marco-indentation method when the grain size is in a range of 18.0 μm to 35.2 μm and the volume fraction porosity is lower than 0.06. Additionally, the grain orientations measured by the EBSD also show no clear correlation with the values of Vickers hardness measured by the micro-indentation method when the porosity of the samples is lower than 0.06. The Vickers hardness, H_V , decreases rapidly as the porosity increases. The total porosity is the dominant factor determining the hardness when it is higher than 0.06. Otherwise, the pore size has a negatively effect on Vickers hardness.

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Table 1 Parameters of the X-ray diffraction instrument

Primary radius (mm)	Secondary radius (mm)	Receiving slit width (mm)	FDS angle (°)	Receiving slit length (mm)	Primary Sollers (°)	Secondary Sollers (°)
173	173	0.2	1	12	2.3	2.3

Figure 1
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Figure 10

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Figure 1 (A) XRD pattern of BSCF powder at room temperature; (B) Particle size distribution of the starting BSCF powder; (C) SEM micrographs of the BSCF powder. The inset on the left corner shows the presence of soft agglomerates.

Figure 2 (A) XRD patterns of BSCF sintered at 1100°C for different periods of dwell time; (B) XRD patterns of BSCF sintered at various temperatures for 10 hours; (C) Lattice parameters as a function of dwell time; (D) Lattice parameters as a function of sintering temperature.

Figure 3 TG results for BSCF powder sintered at different temperatures for 10 hours.

Figure 4 (A) Average grain size of BSCF sintered at 1100 °C as a function of dwell time; (B) dependence of grain size on dwell time at a given sintering temperature 1100 °C; EBSD band contrast micrographs of BSCF sintered at 1100°C for (C) 5 hours, (D) 24 hours and (E) 100 hours.

Figure 5 (A) The average grain sizes of BSCF sintered for 10 hours as a function of sintering temperature; (B) Arrhenius plot of $\ln(\text{average grain size})$ against reciprocal of sintering temperatures for BSCF in this study; (C) data points obtained from the references [6,20,40]; EBSD band contrast micrographs of BSCF sintered at various temperatures for 10 hours: (D) 900°C ; (E) 1050°C ; (F) 1150°C.

Figure 6 (A) relative density of BSCF sintered at 1100°C for various dwell time; (B) Plot of $\log(dp/dt)$ versus $\log(\text{grain size})$ for 1100°C

Figure 7 (A) The Vickers hardness of samples with similar porosity but different grain sizes. The tests were performed with a maximum load of 10 N and the BSCF samples used here were sintered at 1100 °C for 5 to 100 hours; (B) The Vickers hardness as a function of the

inverse square root of the grain size. Note that there is no clear trend of hardness as a function of grain size.

Figure 8 (A) EBSD orientation map of the area where micro-indentation tests were performed; the inset was a typical SEM image of a selected indentation impression without intercepting pores or near grain boundaries; (B) Comparison of load-displacement curves of the indentations made on grains with different orientations shown in (A)

Figure 9 Relatively density (A) and hardness (B) as a function of various sintering temperature. Linear fit of $\ln(\text{hardness})$ against volume fraction porosity according to Equation(7): (C) this study; (D) data points obtained from the references [11,12]

Figure 10 The SEM micrographs of BSCF sintered at different temperatures for 10 hours: (A) 1100°C; (B) 1125°C; (C) 1150°C