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A case study of the effect of Ni substitution on the sintering behaviours of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ oxygen transport membranes

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Abstract

The sintering behaviours of undoped and 8 mol% B-site Ni-doped $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) under various conditions are systematically investigated. All the samples are indexed to be a single cubic phase by X-ray diffraction (XRD). However, second phase NiO particles are identified along the grain boundaries and within the grains of Ni-doped BSCF by energy-dispersive X-ray spectroscopy (EDS). Ni doping increases the lattice parameter of BSCF. The grain size of the undoped BSCF increases from 1.52 to 64.8 μm with increasing sintering temperature from 900 to 1150 $^{\circ}\text{C}$, while the grain size of the Ni-doped counterpart increases from 3.06 to 34.1 μm as the sintering temperature increases from 1000 to 1200 $^{\circ}\text{C}$. The grain growth kinetics is analysed using the expression $D^n = tK_0 \exp(-Q/RT)$. The grain growth

1 exponent n is found to be 3 for the undoped BSCF and 4.7 for the Ni-doped BSCF. The
2 grain growth activation energy (Q) is 650.7 ± 30 kJ/mol for the undoped BSCF and
3 803.4 ± 37 kJ/mol for the Ni-doped BSCF. This indicates that the Ni dopant has a
4 negative influence on densification and grain growth of BSCF.

5 *Keywords: BSCF; Grain growth kinetics; Sintering mechanism; Ni dopant*

6 **1 Introduction**

7 Mixed ionic and electronic conducting (MIEC) ceramics membranes have attracted
8 great attentions recently, because they introduce high ionic and electronic conductivity
9 simultaneously[1]. For this reason, the MIEC materials are used as dense oxygen
10 transport membranes for pure oxygen production[2] or as cathodes for the next
11 generation solid oxide fuel cell[3]. Among these MIEC materials,
12 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) membranes shows a good oxygen permeability at
13 operating temperatures (~ 800 °C) [4], which is primarily ascribed to the high amount
14 of oxygen vacancies in the cubic lattice[5]. However, it has been reported that BSCF
15 membranes undergo undesirable phase transformations (e.g. from cubic to hexagonal)
16 and chemical decomposition during long-term service at operating conditions, which
17 reduces the permeation rate and compromises structural integrity [6]. Therefore, how
18 to optimise the microstructure and chemistry of BSCF to maintain the thermal and
19 mechanical stability and improve the permeability at elevated temperature remains to
20 be overcome.

1 It has been reported that the change of the transit metal radius and the spin transition of
 2 Co^{3+} cause the phase decomposition of BSCF at evaluated temperature [7, 8].
 3 Additionally, the decrease in Young's modulus of BSCF induced by the the spin
 4 transition of Co^{3+} results in mechanical instability at elevated temperatures [9].
 5 Recently, investigators have tried to substitute rare earth metal ions to change the
 6 microstructure in order to optimise the performances of the BSCF-based membranes
 7 [10-15]. A promising solution seems to be the partial substitution of the B-site cations
 8 to minimise the effect of the spin transition of Co^{3+} . For example, Zr doping into the B-
 9 site of BSCF has been reported to improve its mechanical properties [14], although the
 10 oxygen permeation flux decreases considerably with the increase in the content of the
 11 Zr dopant [13]. It has been reported that Ni doping improves the properties of
 12 perovskite-structured $\text{LaFeO}_{3-\delta}$ [16] and $\text{GdBaCo}_2\text{O}_{5+\delta}$ [17]. However, few studies have
 13 been carried out to investigate the effect of Ni doping on the properties of BSCF[18].
 14 Generally, the oxygen permeation flux of perovskite-structured membranes greatly
 15 depends on grain size. For example, the oxygen permeation flux of $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$
 16 decreases with the increase in grain size[19], while the oxygen permeation flux of
 17 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ [20] and BSCF membranes [21] shows an opposite trend.
 18 Therefore, it is certainly worth investigating the microstructure of BSCF and how it
 19 evolves under various sintering conditions. Although there have been considerable
 20 researches on the phase determination and grain growth of BSCF [21-25], there are few
 21 literature reporting the sintering mechanisms or grain growth kinetics of BSCF, not to
 22 mention how Ni doping affects these two aspects. This prompts us to perform the

present study to achieve a comprehensive understanding of the sintering mechanisms and grain growth kinetics of BSCF, as well as the effect of Ni substitution on the sintering behaviours of BSCF.

In this paper, the sintering behaviours of undoped and Ni-doped BSCF are systematically investigated. The effect of Ni doping in BSCF sintered ceramics is studied by means of analysing grain growth kinetic of BSCF, namely the apparent activation energy and the kinetic grain growth exponent. These parameters can be determined from the following equation[26]:

$$D^n = tK_0 \exp\left(-\frac{Q}{RT}\right) \quad (1)$$

where D (μm) is average grain size at the time t ; 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).

2 Experimental procedures

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and 8 mol% Ni-doped BSCF (BSCF-Ni) powders were prepared by a sol-gel method in this study. This method uses metal nitrates, citric acid, and ethylenediaminetetraacetic acid(EDTA) as described in detail elsewhere[27]. The raw materials for BSCF's sol-gel synthesis include $\text{Ba}(\text{NO}_3)_2$ (SigmaAldrich, $\geq 99\%$), $\text{Sr}(\text{NO}_3)_2$ (Sigma-Aldrich, $\geq 99\%$), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 98\%$), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 98\%$) and Na_2CO_3 (Fluka, $\geq 99.999\%$). The raw

materials for BSCF-Ni's wet-chemical synthesis include the nitrate salts of Barium
 [Ba(NO₃)₂], Strontium [Sr(NO₃)₂], Cobalt [Co(NO₃)₂·6H₂O], Iron [Fe(NO₃)₃·9H₂O],
 and Nickel [Ni(NO₃)₂·6H₂O] (Sigma-Aldrich, ≥99%). The raw powder was mixed in
 their stoichiometric ratio in double distilled water and stirred for 24 hours till salts were
 dissolved completely. The powder was then ball-milled in ethanol and calcined at 900
 °C for 10 hours in air in order to remove organic compounds. The first group of the
 undoped BSCF samples was sintered over a temperature range from 900 °C to 1150 °C
 for 10 hours in air and the second group of the undoped BSCF samples was sintered at
 1100 °C for five different periods of time (1, 5, 10, 24, 50 hours). As for BSCF-Ni
 samples, the first group was sintered between 1000 °C and 1200 °C for 10 hours in air,
 and the second group was sintered at 1100 °C for five different periods of time (1, 5,
 10, 24, 50 hours). Both the heating and cooling rates were set to be 180 °C/hour. The
 phase compositions of the BSCF and BSCF-Ni samples were determined by X-ray
 powder diffraction (XRD; PW1830, Philip, Eindhoven, the Netherlands) with Cu K_α
 radiation (λ=0.154 nm) coupled with the Rietveld refinement using the Topas software
 (Bruker) . The detail of the Rietveld refinement can be found elsewhere[28]. The
 densities of the samples were determined from the Archimedes method in distilled
 water. For microstructural observations, all the samples were ground with a series of
 sizes of SiC grinding paper from P400 to P1200, and then polished with diamond paste
 descending from 6 to 0.25 μm. The colloidal silica was used for final polishing (15
 minutes). The microstructure was examined using scanning electron microscopy (SEM;
 Quanta FEG-650, FEI) equipped with electron backscatter diffraction (EBSD,

1 NordlysNano, Oxford Instruments). The grain size was analysed using the area
2 counting technique based on the EBSD maps acquired. The diameter of each grain, D,
3 was calculated by the equivalent area ($D = \sqrt{\frac{4S}{\pi}}$, where D is grain size and S grain area
4 determined by the software).

5 Hardness and Young's modulus measurements were performed by micro-indentations
6 on the polished faces of the samples using a diamond indenter (CSM Instruments,
7 Peseux, Switzerland). The tip geometry and machine compliance were calibrated prior
8 to testing. The tests were done for determining the hardness and Young's modulus values
9 of these materials according to ISO/FDIS Standard 14577-1[29]. A maximum load of
10 10 N was used for micro-indentation test. The procedures of making indentations were
11 followed by a sequence of loading (30 seconds), dwelling at the maximum load (10
12 seconds) and unloading (30 seconds). Two 10×10 indentation matrixes per sample were
13 made, and the distance between the adjacent points was set to be 200 μm, which was
14 more than 5 times the indentation size. Indentations with surface chipping were not
15 included in the analysis. Hardness and Young's modulus were calculated by software
16 (Wilson Tukon 2100, Instron, Germany). Indentation fracture toughness was
17 determined by the direct crack measurement method.

18 **3 Results and discussion**

19 **3.1 X-ray diffraction analysis**

20 Figure 1(A-B) show the XRD patterns of BSCF and BSCF-Ni sintered under various

1 conditions. All samples are indexed to be a single cubic phase with all peaks indexed
2 corresponding to the ICSD card NO.109462[30]. Even at high temperatures, up to
3 1150 °C, the BSCF samples show no decomposition and no other phases can be found
4 by XRD. This means that BSCF exhibits good chemical and structure stability in air
5 within the temperature range and sintering time used in this study.

6 Figure 1(C-D) show the lattice parameters of BSCF sintered under different conditions
7 determined using the Rietveld refinement on the basis of the XRD data. The lattice
8 parameter of the starting powder at room temperature was determined as 3.9790 Å,
9 which is similar to the value reported by Koster *et al.* (3.9830 Å)[31]. As shown in
10 Figure 1(C), the lattice parameter of BSCF increases as the dwell time increases from
11 1 to 10 hour at 1100 °C. A further increase in sintering time from 10 to 50 hours shows
12 negligible effect on the lattice parameter. For a given dwell time (10 hours) shown in
13 Figure 1(D), it can be observed that the lattice parameter almost increases linearly with
14 increasing sintering temperature. Similar findings have also been reported by Wang *et*
15 *al.*[21]. Within the temperature range studied, the maximum variation of the lattice
16 parameters of BSCF is 0.32%.

17 Figure 2 shows the weight change of BSCF sintered between 1000 °C and 1150 °C,
18 with a dwell time of 10 hours at each temperature point. The weight change was
19 monitored using thermogravimetry (TG, SETARAM, K/SETEVO16-1A). The sample
20 was placed in an alumina crucible hung up by a Pt wire in the hot zone the TG chamber.
21 In the whole temperature range covered (between 1000 °C and 1150 °C), it can be

confirmed that the weight of BSCF keeps decreasing. Between 1000 °C and 1100 °C, the weight loss predominantly occurs during the heat-up stage, and there is little weight loss when the samples are held at a certain temperature. Between 1125 °C and 1150 °C, the weight loss is higher than that between 1000 °C and 1100 °C. 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 several other groups [4, 5, 32, 33], the weight loss is mainly connected with the loss of the lattice oxygen. This can cause the formation of oxygen vacancies and the valence change of the transition metal ions. The associated defect reaction can be written in the Kroger-Vink notation as[34]

where M refers to Fe or Co. The weight losses at 1125 °C and 1150 °C are heavier, which suggests that the loss mechanism of the lattice oxygen in this range becomes more active. The loss of oxygen results in the formation of oxygen vacancies. Simultaneously, in order to maintain the charge neutrality, high valence state Fe⁴⁺ and Co³⁺ are changed into Fe²⁺ and Co²⁺, which increases the effective ionic radii and therefore leads to an increase in the lattice parameter [35]. The transformation from Fe⁴⁺ and Co³⁺ to Fe²⁺ and Co²⁺ can be expressed by

1 In sum, the loss of lattice oxygen and the formation of oxygen vacancies can be the
2 reason for the observed increase in lattice parameters with increasing sintering
3 temperature.

4 Figure 3 (A) shows XRD patterns of BSCF-Ni sintered between 1000 °C and 1200 °C
5 for 10 hours. The BSCF-Ni samples are indexed as a cubic perovskite structure. Even
6 up to 1200 °C, the BSCF-Ni samples do not show any decomposition and no other
7 phase can be identified by XRD. As shown in Figure 3(B), it can be observed that the
8 lattice parameter of BSCF-Ni increases approximately linearly with increasing
9 sintering temperature, which is also observed in the undoped BSCF. As only a minor
10 concentration of the Ni dopant has been added to BSCF lattice and the BSCF-Ni has
11 the same crystal structure as BSCF, it is reasonable to believe that, similar to BSCF,
12 BSCF-Ni also suffers from oxygen loss upon exposure to high temperature and it
13 becomes more active as the temperature rises up. The release of oxygen then causes an
14 increase in the lattice parameter with increasing sintering temperature.

15 In addition, compared with the undoped BSCF, Ni doping increases the lattice
16 parameter for a given sintering condition [Figure 3(B) and Figure 1(D)] because the
17 substitution of the larger Ni^{2+} (0.74 Å) cation for the B-site with Fe^{4+} (0.59 Å) and Co^{3+}
18 (0.61 Å) cations. This phenomenon was also observed in Bi-doped [36], Y-doped [37]
19 and Zr-doped BSCF [13, 38] due to the replacement of the larger ionic radius ions.
20 Within the temperature range studied, the variation of the lattice parameters of BSCF-
21 Ni is 0.12%, which is much lower than that of BSCF. This suggests that the sintering

1 temperature has less influence on the lattice parameter of BSCF-Ni than that of BSCF.

2 **3.2 Relative density**

3 Figure 4(A) and Figure 4(C) show the relative densities of the undoped and Ni-doped
4 BSCF as a function of dwell time at 1100 °C. For both types of the samples, the relative
5 densities reach the maximum after 10 hours, although the relative density (95%) for
6 BSCF is higher than that of BSCF-Ni (93.9%). The densities almost stay at a constant
7 with further increase of the dwell time up to 50 hours.

8 Figure 4(B) and Figure 4(D) present the relative densities of both types of the samples
9 as a function of sintering temperature for a given sintering time of 10 hours. As for
10 BSCF, the relative density increases from 73% to 95% as the sintering temperature
11 increases from 900 °C to 1100 °C. Between 1100 °C and 1150 °C, the density shows
12 little change with increasing temperature. As for BSCF-Ni, the relative density
13 gradually increases from 86% to 95% as the sintering temperature increases from
14 1000 °C to 1175 °C. When the sintering temperature reaches 1200 °C, the relative
15 density decreases from 95% to 92.6%. Comparison of the densities of the sintered
16 BSCF-Ni samples sintered between 1175 °C and 1200 °C shows that the linear
17 shrinkage at 1175 °C (9.03%) is higher than that at 1200 °C (8.87%). In other words,
18 the densification rate decreases as the temperature increases from 1175 °C to 1200 °C.
19 The sintering temperature for the maximum density of BSCF-Ni is at a range of 1150 °C
20 to 1175 °C, which is higher than that of BSCF (around 1100 °C).

3.3 Grain growth kinetics

Microstructure of BSCF and BSCF-Ni samples sintered under various conditions are shown in Figure 5 and Figure 6. It is clear observed that for a given dwell time and sintering temperature, the average grain size of BSCF is larger than that of BSCF-Ni. In other words, Ni doping retards grain growth of BSCF during sintering.

The grain growth kinetics [Equation (1)] can be expressed in the form[26]:

$$\ln(D) = \frac{1}{n} \ln(t) + \frac{1}{n} [\ln K_0 - (\frac{Q}{RT})] \quad (5)$$

From the slope ($1/n$) of the $\ln$ (grain size) versus $\ln$ (time) line, the grain growth exponent n can be determined. Figure 7(A) and Figure 7(B) show the isothermal grain growth data for BSCF and BSCF-Ni from 1 to 50 hours at 1100 °C in the form of Equation(4), respectively. The value n of grain growth exponent for BSCF equals 3, which is similar to that obtained by other groups ($n=3.1$)[39]while the value n for BSCF-Ni is calculated to be 4.7.

Figure 7(C) and Figure 7(D) show two Arrhenius plots, in which $\ln(D^n/t)$ is plotted versus the reciprocal of the absolute temperature ($1/T$). Reformatting the Equation (1) yields,

$$\ln\left(\frac{D^n}{t}\right) = -\frac{Q}{R}\left(\frac{1}{T}\right) + \ln K_0 \quad (6)$$

the slope of which can be used for calculation of the apparent activation energy for the grain growth.

1 The grain growth activation energy of BSCF is determined to be 650.7 ± 30 kJ/mol and
2 803.4 ± 37 kJ/mol for BSCF-Ni. Although Salehi *et al.*[22], Baumann *et al.*[23] and
3 Yoon *et al.*[40] did not report an activation energy for grain growth of BSCF, analysing
4 their average grain size data yields an activation energy at a range between 372 and 741
5 kJ/mol, which agrees with the result of BSCF in this study.

6 **3.4 Mechanisms of densification and grain growth**

7 It is a very difficult undertaking to unambiguously identify the controlling mechanisms
8 taking account of the simultaneous occurrence of densification and coarsening
9 processes. Coble *et al.*[34] have proposed a model to determine the controlling
10 mechanism of densification for the final stage of sintering. This model predicts the
11 densification rate $\frac{d\rho}{dt}$ as the following equation:

$$12 \quad \frac{d\rho}{dt} = \frac{CN\xi\gamma_s\Omega}{D^m} \quad (7)$$

13 where ρ represents the density; C denotes a constant; N is the number of pores inside a
14 grain; γ_s refers to the surface energy; Ω denotes volume per cation; D is average grain
15 size to the power m, where m depends on the rate-controlling mechanism for
16 densification; ξ is the relevant diffusion coefficient. For m=3 densification is controlled
17 by lattice diffusion or interface reaction, while for m=4 grain boundary diffusion
18 controls the densification[41]. The m value can be determined by plotting a log-log of
19 Equation (7) in which m equals the slope of the fitting function.

20 The experimental data obtained from the samples sintered at 1100 °C from 5 to 50 hours

1 are plotted in this way for the density above 93% (This density is believed high enough
2 that the sample has reached its final sintering stage). At 1100 °C, the calculated values
3 of m from the plots were 3.98 ± 0.29 for BSCF and 3.57 ± 0.14 for BSCF-Ni, as shown
4 in Figure 8. Considering the values of m , it suggests that the grain boundary diffusion
5 is the dominant controlling mechanism for the densification of BSCF at 1100 °C.
6 However, the predominant mechanism controlling the densification for BSCF-Ni is not
7 clear. It seems that both grain boundary and lattice diffusions are the equally dominant
8 controlling mechanisms for BSCF-Ni at 1100 °C.

9 In the case of grain growth exponent, the value of n for BSCF is determined to be 3. In
10 other words, the grain growth kinetics of BSCF materials do not follow the classical
11 law of parabolic growth ($n=2$). A higher grain growth exponent indicates slowly
12 coarsening grains. It has been reported that the driving force for grain growth is the
13 local curvature of the grain boundary[34]. When the pores are dragged along the grain
14 boundary, it lowers the driving force for grain boundary mobility thereby slowing grain
15 growth[42]. A grain growth exponent greater than 2 can be related to pores and the
16 impurity contained in materials [27, 28]. Therefore, it can be observed in Figure 5 that
17 pores can be the dominant factor for the higher grain growth exponent of BSCF. The
18 grain growth exponent n of BSCF-Ni is determined to be 4.7. It does not also follow
19 the classical law of parabolic growth ($n=2$) either and is higher than that of BSCF. It
20 has been reported [43, 44] that, apart from porosity, a grain growth exponent higher than
21 2 can be also related to the impurity. Examination on BSCF-Ni sintered at 1100 °C for
22 10 hours (Figure 9) shows that apart from the matrix BSCF-Ni, there are small second

1 phase particles (the bright contrast) distributing along the grain boundaries and within
2 the grains. EDS analysis shows that the particles mainly consists of Ni and O, with a
3 atomic ratio of approximately 1:1. This suggests that these second phase particles are
4 NiO. Therefore, both pores and second phase particles can be the dominant factor for
5 the higher grain growth exponent of BSCF-Ni.

6 With regard to the activation energy for grain growth, the activation energy for oxygen
7 ion diffusion (45-105 kJ/mol[45, 46]) is much lower than that for both BSCF and
8 BSCF-Ni. Therefore, cations are believed to be the rate-controlling species of grain
9 growth rather than oxygen ions. Although there is no literature about the activation
10 energy for Ni diffusion in BSCF, it has been reported that the activation energy for Ni
11 diffusion in NiO is 285 kJ/mol [47] which is also much lower than that for the grain
12 growth of BSCF-Ni. This suggests that Ni is probably not the rate-controlling specie of
13 the grain growth of BSCF-Ni. On the other hand, Lein *et al.*[46, 48] have reported the
14 diffusion of Sr/La in $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ is much slower than that of Co/Fe.
15 Therefore, it can be speculated that the Ba/Sr cations can be the rate-controlling species
16 during the sintering process of both the undoped and Ni-doped BSCF.

17 It has also shown above that the apparent activation energy for grain growth of BSCF-
18 Ni ($Q=803.4\pm37$ kJ/mol) is greater than that of the undoped BSCF ($Q=650.7\pm30$
19 kJ/mol). According to Jud *et al.* [49], lattice diffusion usually exhibits a higher
20 activation energy than grain boundary diffusion. On the other hand, the mechanism for
21 the densification of the undoped BSCF is grain boundary diffusion while the

1 densification of BSCF-Ni is equally controlled by grain boundary diffusion and lattice
2 diffusion as discussed before. Therefore, the change in the mechanism results in a
3 higher activation energy.

4 Figure 10(A) shows grain size-density curves for the undoped and Ni-doped BSCF
5 sintered at 1100 °C. The grain size-density curve shows the ratio of the grain growth
6 rate to the densification rate. The slope of the curve for the undoped BSCF lies higher
7 than that for the doped BSCF-Ni, which suggests that the Ni effect is stronger in
8 retarding grain growth than the densification. It also suggests that coarsening in the
9 undoped BSCF seems faster than in the Ni-doped BSCF at this stage. This observation
10 is consistent with the idea that Ni doping inhibits grain boundary mobility at 1100 °C.
11 Additionally, it can be observed that some second phase particles exist along the grain
12 boundaries, although most of particles are located inside the grains. It has been reported
13 that precipitates on the grain boundaries have been shown to have a significant effect
14 in retarding the grain growth even at very low volume concentrations in this range[50].

15 Figure 10 (B-C) show a comparison of the average grain sizes and the ratio of average
16 grain sizes between the undoped and Ni-doped BSCF as a function of sintering
17 temperature. It can be clearly observed that the gap between the average grain size of
18 the undoped BSCF and that of the Ni-doped BSCF becomes larger as the sintering
19 temperature increases. This indicates that the grain growth rate of the Ni-doped BSCF
20 increases by a smaller magnitude compared with that of the undoped BSCF. The ratio
21 of grain size between the undoped and Ni-doped BSCF is 1.04 at 1000 °C, increasing

to 4.64 at 1150 °C. This observation indicates that Ni doping inhibits grain boundary mobility more significantly with increasing sintering temperature between 1000 °C and 1150 °C.

4 Summary

The sintering behaviours of the undoped and Ni-doped BSCF sintered under different conditions have been systematically investigated. All the samples are indexed to be a single cubic phase by XRD. However, second phases (NiO) are identified by EDS in the Ni-doped BSCF. The Ni doping has a negative influence on the densification and grain growth of BSCF. The grain growth kinetic exponent (4.7) for BSCF-Ni is higher than that value of BSCF ($n=3$) because of the introduction of the impurity element and the resistance to the grain boundary mobility caused by the second phase NiO particles. The mechanism for the densification of the undoped BSCF ($m=3.98$) is grain boundary diffusion while the densification of BSCF-Ni is equally controlled by grain boundary diffusion and lattice diffusion ($m=3.57$). The apparent activation energy for BSCF-Ni ($Q=803.4\pm37$ kJ/mol) is also greater than that for BSCF (650.7 ± 30 kJ/mol). It can be speculated that the Ba/Sr cations are the rate-controlling species during the sintering process of both the undoped and Ni-doped BSCF.

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figure 1

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figure 2

figure 8