Microstructure and mechanical properties of 
Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ perovskite-structured oxides doped
with different contents of Ni

Li Wang, 1,* Rui Dou, 2 Yizhe Li, 1 Huanghai Lu, 1 Mingwen Bai, 1 David Hall, 1 Ying Chen 1,*

1School of Materials, University of Manchester, Manchester, M13 9PL, UK
2Technology and Engineering Centre for Space Utilisation, Chinese Academy of Science, Beijing, 10094, PR China
*Corresponding authors at: School of Materials, University of Manchester, Manchester, M13 9PL, UK
E-mail address: li.wang-5@postgrad.manchester.ac.uk (Li Wang)
ying.chen-2@manchester.ac.uk (Ying Chen)

Abstract

Microstructural evolution and mechanical properties of Ba$_{0.5}$Sr$_{0.5}$(Co$_{0.8}$Fe$_{0.2}$)$_{1-x}$Ni$_x$O$_{3-\delta}$ with X=0, 2, 4, 6, 8, 15, 20, and 25 mol% have been systematically investigated. The porosity increases from 4.0% to 17% with increasing the content of Ni doping from 0 to 25 mol%. Meanwhile, the grain size decreases from 22.5 to 5 μm. All the samples are indexed to be a single cubic phase when the Ni doping content is below 25 mol%. Otherwise, secondary phases (NiO) are found along grain boundaries and inside grains. Hardness and Young’s modulus first increase with increasing the content of Ni doping from 0 to 8 mol% and then both decrease with the further increase in the content of Ni doping. The fracture toughness increases with increasing the content of Ni doping from 0 to 20 mol%. However, it decreases with further increasing the content of Ni doping due to the increase in porosity.
Keywords: BSCF; Mechanical property; Microstructure; Ni doping; Secondary phase

1 Introduction

Since $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) membranes have been demonstrated to be with the function of high oxygen permeation rate[1] and to be a high-performance cathode for the next generation of solid-oxide fuel cells by Shao et al.[2], they have attracted significant attentions to be studied. However, how to improve the properties of BSCF including thermal stability, mechanical property and permeability at operating conditions remains to be dealt with. For instance, a phase transition from cubic to hexagonal structure occurs at elevated temperature and reduces the permeation rate of BSCF[3]; additionally, spin transition of Co$^{3+}$ decreases the Young’s modulus of the membrane at elevated temperature, thereby mechanically destabilising the material [4]. Recently, studies have been tried to substitute rare earth metal ions (e.g. Zr, Bi, La and Gd) to modify the microstructure of BSCF-based materials, thereby improving their performances [5-10]. A promising solution seems to be the partial substitution of B-site cations (Fe and Co) to eliminate the effect of spin transition of Co$^{3+}$. It has been reported that Ni doping has been demonstrated to improve different properties of perovskite-structured materials (e.g. $\text{LaFeO}_{3-\delta}$[11] and $\text{GdBaCo}_{2}\text{O}_{5+\delta}$[12]). However, there are few investigations on Ni-doped BSCF. This motivated us to conduct the present study to attain a comprehensive understanding of the effect of Ni substitution on the properties of BSCF.

The permeability of perovskite-structured materials is highly dependent on
microstructure, especially grain sizes. It has been reported that the permeation rate of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ membranes increases with increasing grain sizes[13]. However, the permeation rate of $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ decreases with increasing grain sizes[14]. In the case of BSCF, it has been reported that the oxygen permeation flux increased considerably with the increase of the grain size[15]. Accordingly, it is necessary to investigate microstructural evolution of BSCF, which in return requires a deep understanding of its sintering behaviours. Although there have been considerable researches on the microstructure of BSCF [16-20], there is no literature to report the effect of Ni doping on microstructure of BSCF. To the knowledge of the authors, mechanical properties regarding Ni-doped BSCF have not been also reported yet. In this paper, room temperature mechanical properties including hardness, Young’s modulus and indentation fracture toughness are presented and discussed with correlation to microstructure evolution.

2 Experimental procedures

2.1 Sample preparation

$\text{Ba}_{0.5}\text{Sr}_{0.5}(\text{Co}_{0.8}\text{Fe}_{0.2})_{1-X}\text{Ni}_{X}\text{O}_{3-\delta}$ (BSCF-NiX) powders with $X=0, 2, 4, 6, 8, 15, 20, \text{and } 25 \text{ mol}\%$ were prepared by a sol-gel method in this study. This method used metal nitrates, citric acid, and ethylenediamintetraacetic acid(EDTA) and was described in detail elsewhere[21]. The raw materials for BSCF-NiX sol-gel synthesis include $\text{Ba(NO}_3\text{)}_2$ (Sigma-Aldrich, $\geq 99\%$), $\text{Sr(NO}_3\text{)}_2$ (Sigma-Aldrich, $\geq 99\%$), $\text{Co(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 98\%$), $\text{Fe(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}$ (Sigma-Aldrich, $\geq 98\%$), $\text{Na}_2\text{CO}_3$.
(Fluka, ≥ 99.999%), and Nickel[Ni(NO₃)₂·6H₂O] (Sigma-Aldrich, ≥ 99%). These raw powders were mixed in their stoichiometric ratio in double distilled water and stirred for 24 hours till salts were dissolved completely. The as-received powders were ball-milled in ethanol and calcined at 900 °C for 10 hours in air in order to remove organic compounds and obtain the powder with the final composition. Disc-shaped samples were obtained by uniaxial pressing at a pressure of 100 MPa and were then sintered at 1100 °C for 10 hours in air. Both the heating and cooling rates were set to be 180 °C/h. The samples were then ground with several different sizes of grinding paper from P400 to P1200, and then polished with diamond paste descending from 6 μm to final stage of 0.25 μm.

2.2 Characterisation methods

The phase of all the BSCF-Ni samples was analysed by X-ray diffraction (XRD; PW1830, Philip, Eindhoven, the Netherlands) with CuKα radiation (λ=0.154 nm). The patterns were refined by TOPAS software (Bruker 4.2). The lorentz polarization factor was fixed to 17. The parameter of the instrument was fixed as the following values: Primary radius 173 mm, Secondary radius 173 mm, Receiving slit width 0.2, FDS angle 1, Full Axial Convolution and Filament length 12mm, Sample length 15mm, Receiving Slit length 12mm, Primary Sollers 2.3 and Secondary Sollers 2.3. The background was fit by chebychev polynomials of 3rd order. The peaks were fit using PV_TCHZ function. The refined parameters were zero error, the lattice parameter and crystal size. The cubic phase was refined using Tomkiewicz et al. [22]
structure model based on a cubic cell ($Pm-3m$). The Debye-Waller factor $B$ of oxygen atom was fixed at 1.0 as the insensitivity of laboratory X-ray used in this study. This relatively simple model gives very reproducible results. The error bars of lattice parameters were calculated by the at-least-square fitting during the refinement.

Microstructural evolution was examined using scanning electron microscopy (SEM; Quanta FEG-650, FEI). Grain sizes were analysed by electron backscatter diffraction (EBSD, NordlysNano, Oxford Instruments). The diameter, $G$, of the grain was determined using $G = \sqrt{\frac{4S}{\pi}}$, where $S$ is grain area automatically determined by the HKL Channel 5 software). The porosity was measured by the Image-Pro Plus 6.0 software. Hardness and Young’s modulus measurements were performed by micro-indentations on the polished faces of the samples using a diamond indenter (CSM Instruments, Peseux, Switzerland). The tip geometry and machine compliance were calibrated prior to testing. The practices were done for determining the hardness and Young’s modulus values of these materials according to ISO/FDIS Standard 14577-1[23]. A maximum load of 10 N was used for micro-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 ($\sim 200 \mu m$). Indentations with surface chipping were not included in the analysis. Hardness and Young’s modulus were calculated by software (Wilson Tukon 2100, Instron, Germany). Indentation fracture toughness was determined by direct crack measurement method.
In order to observe crack path below the surface, a focused ion beam (FIB, Quanta 3D, FEI) was used to cut through the crack with an accelerating voltage of 30 kV and a tilt angle of 52 degrees.

3 Results and discussion

3.1 X-ray diffraction analysis

Figure 1 shows typical X-ray diffraction patterns (A) of all the sintered samples and the lattice parameter as a function of the Ni doping content (B). As shown in Figure 1(A), when the content of Ni doping is below 25 mol%, diffraction patterns of BSCF with different contents of Ni doping are indexed by a single cubic phase. For the pattern of BSCF-Ni25, peaks from a secondary phase (NiO) [PDF 47-1049] are identified. For BSCF samples with a low Ni doping level (< 4%), the lattice parameter increases with increasing Ni doping content. When the Ni doping content is above 4 mol%, the lattice parameter shows little change [Figure 1(B)]. It suggests that the solid solubility limit of Ni in BSCF lies in around 4 mol% Ni.

Previous studies have shown the lattice parameters of Bi-doped[24], Y-doped[25] and Zr-doped BSCF [8, 26] increase with increasing doping content to a certain level due to the replacement of the larger ionic radius ions. It has been also found in LaCoO3 [27] that the lattice parameter increases with increasing Ni substitution of Co in a certain content range, because the ionic radius of Ni2+ is larger than that of Co3+. On the other hand, as for La-doped in BSCF[28], the lattice parameter decreases with
increasing the La doping level because of the substitution of smaller La\(^{3+}\) cations. Therefore, the lattice parameter significantly depends on the radii of substitution ions. In the case of Ni-doped BSCF, the lattice parameter increases with increasing the Ni doping content because the substitution of larger Ni\(^{2+}\) (0.74 Å) cation for the B-site with Fe\(^{4+}\) (0.59 Å) and Co\(^{3+}\) (0.61 Å) cations.

### 3.2 Grain evolution

Figure 2 shows EBSD band contrast micrographs of BSCF with different Ni doping contents (2, 4, 15, 20 mol\%) sintered at 1100 °C for 10 hours. It is clearly observed that a secondary phase (denoted by the red arrows in (C) and (D)) exists in BSCF doped with 15 and 25 mol\% Ni. According to the EDS spectrum of the secondary phase (Figure 3), the atom ratio between Ni and O is approximate to 1, which suggests that secondary phases can be NiO.

Figure 4 shows the average grain size as a function of the Ni doping content in BSCF (BSCF-NiX, X=0, 2, 4, 6, 8, 15, 20, 25 mol %). It is clearly observed that the average grain size of Ni-doped BSCF decreases with increasing the Ni doping content. The grain size reduces gradually with increasing Ni doping content up to 4 mol\%; and then the reduction rate slows down with the further increase in the Ni doping content. This indicates that the Ni doping affects the grain growth of BSCF through two mechanisms. As reported by Garcia \textit{et al.}\[29]\, the decrease in grain size is mostly likely related to the impurity content. In the case of Ni doping in BSCF, it can refer to about the solute (Ni\(^{2+}\)) into lattice and precipitated phase (NiO), which is discussed
In the range of Ni doping from 0 to 4 mol%, it can be concluded that the grain size decreases with increasing the doping content due to Ni doped into the lattice as no secondary phase has been found. A possible reason for this effect is because Ni doping retards the diffusion of other ions, thereby constraining grain growth. This phenomenon has also been found in a Ni-doped BaTiO$_3$[30].

In the range of Ni doping from 4 to 25 mol%, apart from the constraint from Ni$^{2+}$ solute in the BSCF lattice, the decrease of the grain size with increasing the doping content can be also caused by precipitation of the secondary phase which constrains grain growth. It can be clearly observed in Figure 5 that NiO particles distribute both inside the grain and along the grain boundaries. Furthermore, with increasing the Ni doping content, the number of particles increases. Under the same sintering conditions(1100 °C, 10 hours), the grain size for BSCFNi-25 is a factor 4.5 smaller in comparison with that of the pure BSCF as shown in Figure 4. This phenomenon is also observed in BSCF with Zr-doping[26]. According to the explanation from Stournari et al.[26], the suppressed grain growth in Zr-doping BSCF can be ascribed to secondary phase pinning or dragging mechanism, because small Zr-rich crystallites can be found along the grain boundaries. Therefore, it suggests that the secondary-phase NiO particles have similar effect in constrain the grain growth of BSCF.

It can be also clearly observed that the number of secondary phase particles (NiO)
locating in the grain boundaries increases with increasing the Ni doping content, especially above 15 mol%, as shown in Figure 2(C-D). As mentioned above, secondary phase particles can inhibit grain growth by pinning or dragging the migration of grain boundaries, which is often called the Zener pinning or drag[31, 32]. The total pinning force $F_{TP}$ is given by

$$F_{TP} = \frac{3fy_b \sin \theta \cos \theta}{r}$$  \hspace{1cm} (1)

where $f$ is the volume fraction of particles at the grain boundaries, $\gamma_b$ the grain boundary energy per unit area, $\theta$ the angle between the grain boundary surface and the point of intersection with particle, and $r$ is the particle radius. These parameters $f$ and $r$ were determined by Image analysis based SEM micrographs (Image-Pro Plus 6.0 software). With increasing in the Ni doping level, the volume fraction of the secondary phase particles increases, and since the particle radius changes only slightly, the total pinning force of the secondary phase particles increases according to Equation(1). Therefore, the grain size gradually decreases.

The first quantitative model to describe the effect of inclusion particles on the grain growth in polycrystalline materials was developed by Zener et al.[33, 34]. In their model, the limiting grain size $G$ of the main phase is given by:

$$G = \frac{2d}{3f}$$  \hspace{1cm} (2)

where $d$ is the average size of the particles. Zener’s model involves two major assumptions: one is the existence of a stabilised microstructure, in which grain growth
stops or a constant grain/particle size ratio prevails during extended heating; the other
is that isolated spherical inclusion are randomly dispersed in the matrix. Since many
experimental results showed that the observed limiting gram sizes were not in
agreement with those predicted by Zener’s equation, modified models have been
proposed. The general form of the modified equation is [35-37]

\[
G = C \frac{d}{\gamma_m}
\]

(3)

\[
\log \left( \frac{C}{d} \right) = -m \log (f) + \log (C)
\]

(4)

where C and m are constants.

To evaluate the Zener’s effect, the value of C and m can be determined from the
experimental data by plotting log (G/d) versus log (f) and compared with the ones
predicted by the models. Since these models are based on a preferential location of the
secondary phase particles at the grain boundaries, samples with Ni doped above 15
mol% were used. The data of these three different doping levels are shown in Figure 6.
From this plot, the obtained values of C and m are 0.94 and 0.55, respectively. These
values do not agree well with the original Zener’s model(C=0.67, and m=1), but they
are in close agreement with the ones in the modified models of Haroun and Budworth
(C=1.03 and m=0.5)[35] and Gladman et al.(C=0.88 and m=0.5)[36].
3.3 Grain size distributions and grain aspect ratio distributions

Figure 7 shows grain size distributions and grain aspect ratio distributions of sintered BSCF with various Ni doping contents sintered at 1100 °C for 10 hours. It has been reported that dopant can induce abnormal grain growth in some ceramics systems [38-41]. As shown in Figure 2, all the samples of Ni-doped BSCF show regular equiaxed grains and no abnormal grain growth can be found. As shown in Figure 7(A), the shape of the grain size distribution profile remains essentially similar while the grain size distribution curves shift toward the finer end of the size profile as the Ni doping content increases. This phenomenon is also found in other doped ceramic systems [42-44].

From the literature [45, 46], it has been proved that doping also can influence the grain aspect ratio of ceramics materials. However, the grain aspect ratios of BSCF doped with different content Ni are approximately 1.8 and are almost the same as those of pure BSCF.

3.4 Porosity

Figure 8 shows the dependence of porosity of BSCF on the Ni doping content. It is clearly observed that the porosity increases with increasing the Ni doping content. In other words, Ni doping clearly inhibits densification of BSCF at 1100 °C. With increasing Ni doping concentration from 2 to 8 mol%, the porosity increases gradually.
However, with further increasing the dopant concentration up to 25 mol% the porosity increases abruptly and the porosity of the BSCF with 25 mol% doping is around twice higher than that with 15 mol% doping, which is attributed to the increase in the amount of secondary phase NiO. In sum, the densification rate of BSCF is reduced by the Ni doping, and the reduction rate increases with the increase in Ni doping level. This phenomenon indicates that the diffusion rate and/or the sintering stress were reduced by Ni doping.

The dissolution of Ni into BSCF lattice leads to a decrease of diffusion coefficient of the cations by depressing the concentration of this species. Studied on Ni doped in BaTiO$_3$[30] have shown that Ni constrains the diffusion rate of Ti. Additionally, Ti is the rate controlling species due to its the highest activation energy of diffusion in BaTiO$_3$[30]. Therefore, Ni doping retards the densification of BaTiO$_3$[30]. Similarly, in the case of Ni-doped in BSCF, it suggests that one reason for the increase in the porosity with increasing Ni doping content can be attributed to the diffusion of cations constrained by Ni.

With respect to the process of sintering, the densification occurs by means of the pore surface moving to the pore centre. Very small inclusions will be possibly dragged and gathered together with the aid of the movement of pore surfaces during the sintering[42]. The force of these particles obstructing the movement of the surface is equivalent to the influence of inclusions on the grain boundary mobility[42]. In this way, the drag effect of the particles on the pore-surface motion consequently
decreases the sintering stress. Therefore, besides restraining the diffusion rate, Ni doping can retard the densification of BSCF by reducing the sintering stress.

3.5 Hardness and Young’s modulus

Figure 9 shows the hardness and Young’s modulus as a function of Ni doping contents in BSCF sintered at 1100 °C for 10 hours. It is clearly observed that both hardness and Young’s modulus show a non-monotonous trend with Ni doping content. In a lower doping level (0 to 8 mol%), they increase with Ni doping content, while at a higher doping level (8 to 25 mol%), they decrease with increasing Ni doping content.

As mentioned before, Ni doping causes an increase in the lattice parameter, an increase in porosity, and an increase in the amount of secondary phase but a decrease in grain size. In the case of hardness of Ni-doped BSCF, the increase from 0 to 4 mol% is probably caused by the strain induced by lattice distortion, because the ionic radius of Ni$^{2+}$ is larger than those of both Fe$^{4+}$ and Co$^{3+}$[30]. Ling et al.[47] have also found this phenomenon in other perovskite-structured materials and have attributed it to a solute solution strengthening mechanism. From 4 to 8 mol%, the increase in hardness of Ni-doped BSCF is due to formation of secondary phase, because the hardness of a secondary phase (NiO) is much higher than that of pure BSCF and the amount of secondary phase increases. Between 8 and 25 mol%, the reduction in hardness may be due to the fast increase in the porosity. Although the amount of secondary phase increases with increasing the Ni doping level, the porosity of Ni-doped BSCF shows an even more dramatic increase at this range. Therefore it is suggested that the
hardness of secondary phases cannot compensate the loss caused by the increase in porosity.

With respect to the Young’s modulus of Ni-doped BSCF, the curve shows a similar trend with that of hardness. As reported in the literature [48-50], doping can result in the change in bond length thereby changing bond energy. And the Young’s modulus significantly depends on the bond length and bond energy[49, 50]. It has been reported that Ni-O bond energy (392 kJ/mol) is higher than that of Co-O bond (368 kJ/mol)[51]. Therefore, the increase in bond length and bond energy can be the reason for the increase in Young’s modulus. From 4 to 8 mol% the increase in Young’s modulus can be attributed to secondary phase particles, because the Young’s modulus of secondary phase particles NiO (263 GPa)[52] is much higher than that value of BSCF (80 GPa)[53] and the amount of secondary phase increases. Between 8 and 25 mol%, the reduction in Young’s modulus is due to the sharp increase in porosity, since Young’s modulus is sensitive to the porosity[54].

3.6 Fracture toughness

Figure 10 shows the indentation fracture toughness of BSCF doped with different contents of Ni. It is clearly observed that Ni doping increases the fracture toughness compared with pure BSCF. There are three possible factors to explain this phenomenon. Firstly, Ni doping increases the Young’s modulus when the content is below 8 mol%. A higher Young’s modulus would lead to higher fracture toughness, with other properties unchanged. Secondly, the fracture toughness of NiO(1.65
MPa·m$^{0.5}$) [55] is larger than that of pure BSCF. Thirdly, crack deflection by secondary phases results in the increase in the fracture toughness.

From 0 to 4 mol%, the increase in fracture toughness of Ni-doped BSCF can be ascribed to the increase in Young’s modulus. From 4 to 8 mol%, the increase is attributed to the larger fracture toughness of the secondary-phase NiO particles. In addition, the amount of secondary phases increases with increasing the content of Ni-doping. As shown in Figure 11, no substantial crack deflection was found and crack propagation was primarily transgranular as for BSCF-Ni8.

As shown in Figure 12, the secondary phase in Ni-doping samples can serve to deflect cracks for BSCF-Ni20 and results in a modest enhancement in fracture toughness, while straight crack pass though the grains for BSCF with less than 8 mol% Ni doping. This phenomenon also can be observed in other perovskite-structured materials [56-58]. Between 20 and 25 mol%, the reduction in fracture toughness is probably due to the increase in the porosity.

Figure 13 shows EDS mapping of secondary phase adjacent to the crack in BSCF-Ni20 and NiO can be identified. The direction of the crack propagation has been changed, as shown in Figure 12, which is believed to be affected by the thermal internal stress due to the thermal expansion mismatch between the matrix and the NiO particles. Because of the different thermal expansion coefficients (TEC) of the BSCF matrix and NiO, the thermal residual stress is produced between matrix grains and the NiO particles when the samples were cooling from the sintering temperature (1100 °C).
to room temperature. Assuming all particle inclusions are spherical, the residual stress can be determined by the equation derived by Selsing:[59]

\[
\sigma = \frac{(\alpha_m - \alpha_p)\Delta T}{2E_m \left(1 + \frac{1 - 2\nu_p}{E_p}\right)}
\]  

(5)

where \( \alpha_m \) and \( \alpha_p \) are the thermal expansion coefficient (TEC) of the matrix and the particle, respectively. \( \Delta T \) is the temperature change; \( E \) and \( \nu \) are the Young’s modulus and Poisson’s ratio respectively. In this study, the TEC of matrix and NiO particles are 19.7\times10^{-6} \text{ and } 17.1\times10^{-6} \text{ °C}^{-1}, \text{ respectively}[60]. The Young’s modulus and Poisson’s ratio for polycrystalline NiO are 263 GPa and 0.37, respectively[60]. The value of thermal residual stress is found to be 233 MPa in tension in the radial direction and 117 MPa in compression in the tangential direction at the interface of the matrix/NiO particles. Crack propagation can bypass the NiO particles induced by the thermal residual stress.

As shown in the Figure 14, it can be observed crack deflection induced by secondary phase under the surface. Therefore, the increase in fracture toughness can be attributed to crack deflection[57]. This phenomenon was also found in Ni doping in other ceramic materials[52].

4 Summary

The sintering behaviours and mechanical properties of BSCF doped with different contents of Ni sintered at 1100 °C for 10 hours have been systematically investigated. All the samples are indexed to be a single cubic phase by XRD when the Ni doping
content is lower than 25 mol%. Otherwise, secondary phases (NiO) are identified by XRD, which agrees with the results determined by EDS. The grain size of BSCF decreases with increasing the content of Ni doping while the porosity increases with increasing the content of Ni doping. Hardness and Young’s modulus increase with increasing the content of Ni doping from 0 to 8 mol%, because of the lattice distortion strain caused by the solute Ni$^{2+}$ and the precipitation of the secondary-phase NiO. Otherwise, they both decrease with increasing the content above 8 mol% due to the increase in the porosity. The indentation fracture toughness increases with increasing the content of Ni doping from 0 to 20 mol%, because the content of secondary phase increases and crack deflection is found. However, it decreases with further increasing the content of Ni doping due to the increase in the porosity.

**References**

1. Tan, L., et al., Influence of sintering condition on crystal structure, microstructure, and oxygen permeability of perovskite-related type $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes. Separation and purification technology, 2003. 32(1): p. 307-312.


3. Yi, J., et al., High-temperature compressive creep behaviour of the perovskite-type oxide $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$. Solid State Ionics, 2009. 180(36-39): p. 1564-1568.

4. Huang, B., et al., Anomalies in the thermomechanical behavior of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ceramic oxygen conductive membranes at intermediate temperatures. Applied Physics Letters, 2009. 95: p. 051901.

5. Yang, J., et al., Bismuth doping effects on the structure, electrical conductivity and oxygen permeability of $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ ceramic membranes. international journal of hydrogen energy, 2012. 37(12694): p. e12699.

6. Li, Z., et al., Evaluation of (Ba$_{0.5}$Sr$_{0.5}$)$_{0.85}$Gd$_{0.15}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ cathode for intermediate temperature solid oxide fuel cell. Ceramics International, 2012. 38(4): p. 3039-3046.

9. Pećanac, G., et al., Comparison of thermo-mechanical characteristics of non-doped and 3mol% B-site Zr-doped Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$. Ceramics International, 2014. 40(1): p. 1843-1850.
10. Kang, B.-K., et al., Thermal expansion behavior of La-doped Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ cathode material. Ceramics International, 2013. 39(7): p. 8267-8271.
13. Martynczuk, J., M. Arnold, and A. Feldhoff, Influence of grain size on the oxygen permeation performance of perovskite-type (Ba$_{0.5}$Sr$_{0.5}$)(Fe$_{0.8}$Zn$_{0.2}$)O$_{3-δ}$ membranes. Journal of Membrane Science, 2008. 322(2): p. 375-382.
15. Wang, H., et al., Investigation of phase structure, sintering, and permeability of perovskite-type Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ membranes. Journal of membrane science, 2005. 262(1): p. 20-26.
17. Baumann, S., et al., Influence of sintering conditions on microstructure and oxygen permeation of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (BSCF) oxygen transport membranes. Journal of Membrane Science, 2010. 359(1): p. 102-109.
18. Klande, T., O. Ravkina, and A. Feldhoff, Effect of microstructure on oxygen permeation of Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ and SrCo$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ membranes. Journal of the European Ceramic Society, 2013. 33(6): p. 1129-1136.
19. Wang, H., et al., Investigation of phase structure, sintering, and permeability of perovskite-type Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ membranes. Journal of Membrane Science, 2005. 262(1): p. 20-26.
20. Tan, L., et al., Influence of sintering condition on crystal structure, microstructure, and oxygen permeability of perovskite-related type Ba$_{0.8}$Sr$_{0.2}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ membranes. Separation and purification technology, 2003. 32(1): p. 307-312.
22. Tomkiewicz, A.C., et al., Evidence for the low oxygen stoichiometry of cubic Ba$_{0.5}$Sr$_{0.5}$Co$_{0.5}$Fe$_{0.5}$O$_{5-δ}$ from in-situ neutron diffraction. Solid State Ionics, 2013. 253: p. 27-31.

24. Yang, J., et al., Bismuth doping effects on the structure, electrical conductivity and oxygen permeability of Ba 0.6 Sr 0.4 Co 0.7 Fe 0.3 O 3− δ ceramic membranes. International Journal of Hydrogen Energy, 2012. 37(17): p. 12694-12699.


26. Stournari, V., et al., Creep behavior of perovskite-type oxides Ba0.5Sr0.5(Co0.8Fe0.2)1−xZrxO3−δ. Journal of the European Ceramic Society, 2015. 35(6): p. 1841-1846.


28. Kim, J., et al., Chemically Stable Perovskites as Cathode Materials for Solid Oxide Fuel Cells: La - Doped Ba0.5Sr0.5Co0.8Fe0.2O3−δ. ChemSusChem, 2014. 7(6): p. 1669-1675.


49. Wang, Y., F. Yang, and P. Xiao, Role and determining factor of substitutional defects on thermal conductivity: A study of La₂(Zr₂⁻ₓBₓ)O₇ (B= Hf, Ce, 0≤ x ≤ 0.5) pyrochlore solid solutions. Acta materialia, 2014. 68: p. 106-115.


Figure 3

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>50.61</td>
</tr>
<tr>
<td>Fe</td>
<td>0.31</td>
</tr>
<tr>
<td>Co</td>
<td>3.15</td>
</tr>
<tr>
<td>Ni</td>
<td>45.09</td>
</tr>
<tr>
<td>Sr</td>
<td>0.18</td>
</tr>
<tr>
<td>Ba</td>
<td>0.66</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 7

(A) Cumulative frequency undersize/\% vs. Log(grain size/μm)

(B) Cumulative frequency undersize/\% vs. Grain aspect ratio
Figure 1(A) XRD patterns of different contents of Ni-doped BSCF; (B) Lattice parameter as a function of Ni doping content. The line is a guide to eye.

Figure 2 EBSD band contrast micrographs of sintered BSCF with different Ni contents: (A) 2 mol%; (B) 4 mol%; (C) 15 mol%; (D) 20 mol%. The red arrows in (C) and (D) mark the secondary phase NiO particles.

Figure 3 EDS spectrum of secondary phase of Ni-doped BSCF.

Figure 4 Average grain sizes of Ni-doped BSCF as a function of the Ni doping content.

Figure 5 Microstructure of BSCF doped with 6 mol%(A) and 8 mol%(B) Ni sintered at 1100°C for 10 hours.

Figure 6 log(G/d) as a function of log(f) for the sample of BSCF doped with 15, 20, 25 mol% Ni sintered at 1100°C for 10 hours.

Figure 7 Grain size distributions (A) and grain aspect ratio distributions (B) of sintered BSCF with various Ni doping contents.

Figure 8 Porosity as a function of the Ni doping content of BSCF sintered at 1100°C for 10 hours.

Figure 9 Hardness and Young’s modulus as a function of Ni doping contents. Solid lines are an eye-guidance.

Figure 10 Indentation fracture toughness as a function of different Ni doping contents. Solid line is an eye-guidance.

Figure 11 Typical indentation impression of BSCF-Ni8.

Figure 12 SEM micrographs of crack induced by Vickers indentation for BSCF-Ni20. (The inserted micrographs show the high magnification of cracks).

Figure 13 EDS mapping of secondary phase adjacent to the crack in BSCF-Ni20. Red arrow points out the secondary phase NiO.

Figure 14 SEM image of the FIB-milled region BSCF-Ni20, where crack path below the surface has been exposed.