

Preparation of dense $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes: Effect of Ba^{2+} substituents and sintering method to the density, hardness and thermal expansion coefficient of the membranes

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Received: 16 June 2016, Revised: 28 November 2016 and Accepted: 12 December 2016

DOI: 10.5185/amlett.2017.6948
www.vbripress.com/aml

Abstract

The aims of this research are to study the sintering technique during the production of $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) membranes and to obtain information about the correlation between Ba^{2+} substituent with membrane's density, hardness and thermal expansion coefficient. BSCF with $x = 0.5, 0.6$ and 0.7 (BSCF 5582, 6482 and 7382) were synthesized by the solid state method. X-ray diffraction analysis revealed that the three oxides possessed a cubic structure with high purity and crystallinity. BSCF membranes were made by dry pressing method from their respective powders which passed through 400 mesh sieves at 1050 °C and 1150 °C. Membranes with high density were obtained from phased sintering technique at 1150 °C. SEM analysis results showed that the surface of the membranes is dense, albeit pores can still be found in the cross section of the membranes. The density of the membranes decreased as the amount of Ba^{2+} substituent increases indicated by the increase in pore size. A similar pattern was also found in the membrane hardness which decreased as the amount of Ba^{2+} content increased. Thermal expansion coefficient of BSCF 5582 was 18.28 ppm which was the highest one followed by BSCF 6482 and BSCF 7382. Copyright © 2017 VBRI Press.

Keywords: $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, dense membranes, perovskite, sintering, thermal expansion.

Introduction

Mixed Ionic and Electronic Conducting Membranes (MIEC) is a type of membrane which can be used in the process of natural gas conversion, such as methane to liquid fuel through methane partial oxidation [1]. The ability of converting natural gas is caused by the vacancy of oxygen ion inside the crystal lattice of the membrane material, hence making it possible for oxygen ion to diffuse in the void of oxygen. In the application of oxygen-ion conductor, the membranes must be dense so that the oxygen only diffuses in the form of its ion (O^{2-}) and not in the form of oxygen molecules (O_2). Hence controlling the amount of oxygen to be reacted with natural gas can be done perfectly [2]. Besides from being dense, the membranes must also be strong so that the reaction control can be maintained. One type of MIEC membrane material which has the potential to be

developed to undergo the reaction of methane partial oxidation is the strontium-cobalt-iron based perovskite oxide, or $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (SCF 182), because it is known to have high oxygen permeability. However, such oxide is known to have low structure stability, particularly when it is exposed to a reducing atmosphere where the methane partial oxidation reaction takes place. The low structural stability is what caused the SCF 182 to be easily reduced to form another phase by the reducing gases [3]. The structural stability can be increased by substituting Sr^{2+} with Ba^{2+} which in turn produced $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF). Babakhani and co-workers [4] reported that the best structure stability was obtained when substituting Ba^{2+} by as much as 0.3 to 0.7.

Although the BSCF membranes have better structure stability compared to the SCF, the existence of Ba^{2+} ion inside the material can affect the characteristics of the membranes being produced, particularly their mechanical

properties. The Ba^{2+} has a lower melting point compared to the Sr^{2+} , which means that this can alter the mechanical properties of the membranes that have relations to density, hardness and heat expansion [5]. The lower melting point of Ba^{2+} compared to Sr^{2+} also caused a difference in the membrane sintering behavior, where the existence of Ba^{2+} caused the membranes to be sintered at a lower temperature. This process will have effects towards the density level of the membranes at certain sintering temperatures [6]. Huang and co-workers [5] also reported that the existence of Ba^{2+} can reduce the hardness of the membranes and increase the heat expansion of the BSCF membranes, especially when exposed to high temperatures.

The aforementioned mechanical properties become important factors during the process of methane partial oxidation, because the oxidation reaction is generally carried out at temperatures higher than 700 °C. Porous membranes will cause the molecular oxygen to diffuse through the membrane pores. In the meantime, membranes with low level of hardness are more prone to experience cracks which in turn will create gaps within the membranes. Moreover, the incompatible heat expansion between the reactor materials and the membrane will cause cracks on the reactor joints and hence causing a leak of oxygen gases. The leak of oxygen gases caused the oxygen that reacted with methane to be uncontrollable. Therefore, information regarding the mechanical properties of the BSCF membranes, particularly their density, hardness and heat expansion, are important factors and must be studied in detail.

The physical properties of BSCF such as hardness and heat expansion have not been studied in depth. A research on the hardness of membranes was reported by Chanda and co-workers [7] by focusing on the BSCF 5582 membrane. The result obtained showed that the hardness of a membrane is affected by the membrane temperature during the measurement, in other words, the hardness of the membrane depends on its temperature. Whilst Patra and co-workers [8] have been studying the heat expansion of the BSCF membranes with temperatures of up to 800 °C, and reported that the release of oxygen from the lattice had more effects towards the heat expansion pattern compared to the amount of Ba^{2+} substituents.

According to the previous explanations, it can be seen that partial substitution of Sr^{2+} with Ba^{2+} caused a change in the sintering characteristics and mechanical properties of the resulted BSCF membranes, particularly its density, hardness and heat expansion. Due to these facts, the sintering technique and temperature are needed to be studied in more details in order to obtain the right conditions in preparing the BSCF membranes and to obtain the information regarding the correlation of the amount of Ba^{2+} substituent with its mechanical properties. This research was focused on the BSCF membranes with $x = 0.5$ to 0.7 (BSCF 5582, BSCF 6482 dan BSCF 7382) because this range lies on the composition range which has the best structure stability [4].

Experimental

Materials

Powder form of p.a. grade chemicals were used in the preparation of BSCF powders and membranes. The chemicals were lanthanum (III) oxide (La_2O_3 p.a 99.5%, Merck), barium carbonate ($BaCO_3$ p.a 99.5%, Merck), cobalt oxide (Co_3O_4 p.a 99.5%, Aldrich), strontium nitrate ($Sr(NO_3)_2$ p.a 99.0%, Merck), and iron (III) oxide (Fe_2O_3 p.a 97%, Merck).

Synthesis of BSCF 5582, 6482, and 7382 perovskite oxide

BSCF 5582 ($Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$), BSCF 6482 ($Ba_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$) and BSCF 7382 ($Ba_{0.7}Sr_{0.3}Co_{0.8}Fe_{0.2}O_3$) were synthesized from their respecting metal oxides and nitrates by using solid state method as reported by Utomo et al. [9]. All raw materials were firstly dried in an oven for an hour at 105 °C, and then they were left to cool down in a desiccator for 30 minutes before weighing them to match their stoichiometric amount. After that, the reactant mixture was ground with porcelain mortar and pestle for 2 hours producing precursors. The precursors were then calcined in a muffle furnace by increasing the temperature gradually, starting from room temperature up to 400 °C and continued to 890 °C, and kept constant for 2 hours. This process was repeated twice with the process of intermediate grinding for 15 minutes. The powder that was obtained from this process was re-calcined at 1050 °C for 2 hours. The calcination process was carried with a heating rate of 3 °C.min⁻¹.

The synthesized BSCF powders were characterized by using Philips X'Pert PN-1830 diffractometer in the Laboratory of Energy ITS. The analysis were carried out using Cu K α radiation ($\lambda = 1,5406 \text{ \AA}$) at $2\theta = 5$ to 100° with an interval of 0.02° and a speed of $0.4^\circ.s^{-1}$. The diffractograms were then matched with the standard data of the BSCF 5582 which can be seen in the PDF card (Powder Diffraction File) number 01-075-6980 issued by JCPDS in 2012.

Preparation and characterization of the BSCF dense membrane

The dense membranes were made by using dry pressing method, with the initial diameter of 13 mm and thickness of 2 mm. The synthesized perovskite oxide powders were sieved using 400 mesh test sieve to get particle size of $\leq 37 \mu m$. The molding was done by applying a load of 4 tons for 15 minutes. The green membranes resulted from the molding process were then sintered at 890 °C for 2 hours with the heating rate of 3 °C.min⁻¹ using muffle furnace. The membranes produced were re-sintered at 1050 °C or 1150 °C for 4 hours with the same rate of temperature increase using high temperature furnace.

The shrinkage of membranes from the sintering process was determined by measuring the diameter and the thickness of the membranes by using calipers before and after sintering. The shrinkage was calculated using Equation 1.

$$\text{Shrinkage} = \frac{\text{Vol.}_{\text{initial}} - \text{Vol.}_{\text{end}}}{\text{Vol.}_{\text{initial}}} \times 100\% \quad (1)$$

The initial test of the membrane density after sintering was done by using the water droplets method. Water was being dripped on top of the sintered membrane surface using syringe and was left idle for 10 minutes. If the water droplets were not absorbed then it can be said that the membrane is a dense membrane.

Characterization by SEM (Zeiss EVO MA-10) was carried out to observe the density level of the surface and the cross section of the membranes. Before being analyzed, the surface of the sample was coated with Pd/Au to increase the conductivity.

The membranes with the highest level of density, based on SEM analysis results, were then measured their hardness by using Vicker's Microhardness Tester and their thermal expansion coefficient by using TMA (TMA/SDTA 840 METTLER TOLEDO). Characterization of the membrane hardness was carried out at room temperature with a load of 0.5 kgf and a loading period of 10 seconds. Indentations were taken on 5 different points, which is done in order to obtain an accurate data that could represent the overall hardness of the membrane. Characterization with TMA was carried out with a load of 0.02 N at temperature range between 25 °C and 1000 °C and a rate of 10 °C.min⁻¹.

Results and discussion

Synthesis and characterization of BSCF powders

X-ray diffraction analysis results of the synthesized BSCF powder are shown in **Fig. 1**. The results of the three BSCF diffraction patterns were matched with the 2012 JCPDS database and showed a similar pattern as the pattern of BSCF 5582 shown on the PDF card No. 01-075-6980 which has a cubical unit cell. The matching results showed that the three synthesized powders have formed a perovskite phase with a high level of purity and crystallinity. The high level of purity was indicated by the undetected peaks of other phases except for the perovskite phase and the flat baseline, whilst the crystallinity was seen from the sharpness and the height of peaks intensity. No secondary phase was detected in the diffraction pattern of each perovskite (BSCF 5582) under the diffraction analysis condition. When there is a secondary phase, X-ray diffraction pattern will show the diffraction peaks of the secondary phase as reported by Bonturim *et al.* [9] for provskites made by sol-gel method at various pH condition.

The purity and crystallinity of BSCF made by a simple solid state method are comparable to the sol gel method as reported by Bonturim *et al.* [9]. In the sol gel method, the change in pH during the sol-gel reaction may cause the formation of secondary phase which was not found when the BSCF were synthesized by the solid state method. From the diffractograms shown in **Fig. 1**, it can be noticed that the diffraction peaks shifted to lower 2θ as the substituent amount of Ba²⁺ increases. The shifting in diffraction peaks towards the lower angle of 2θ showed that there was an increase in the interplanar distance on

the crystal lattice [10]. The increase of the interplanar distance indicated that there was an increase in the distance between ions in the BSCF crystal. As a result, this weakened the strength of the bonds between the ions, particularly the bonds between the metal ions (cobalt and/or iron) with the oxygen. The analysis results of the X-Ray diffraction showed that the interplanar distance increased as the amount of Ba²⁺ substituents decreased.

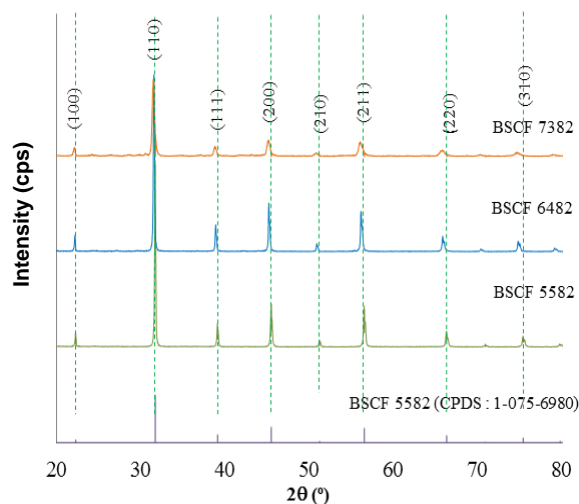


Fig. 1. The X-Ray diffractograms of the synthesized powder.

Dense membranes preparation and properties

Dense membranes used in this work were made from synthesized BSCF 5582, 6482 and 7382 powders that have been filtered using a 400mesh sieve (which produced particle size ≤ 37 μm). This uniform particle size is needed to produce membranes with a density high enough to undergo the process of sintering. The dense green membranes ease the process of sintering as reported by Das and co-workers [11].

The molding of the membranes was done by using dry pressing method. This method was chosen because it is capable of producing membranes with very high density and can be sintered directly. The BSCF powder was pressed by applying a load of 4 tons for as long as 15 minutes inside a 13mm diameter membrane mold. The membranes that were produced were then called as green membranes.

The sintering process had significant effects towards the density of the membranes being produced. In general, the higher sintering temperature, the higher membranes density. Utomo *et al.* [12] reported that the BSCF 5582 began to sinter above 1000 °C and began to melt at 1200 °C. Therefore in this research, the temperatures were varied between 1050 °C and 1150 °C with a sintering period of 4 hours in order to find out the effects of sintering temperature towards the density of the membranes.

Prior to sintering the green membranes at 1050 °C or 1150 °C, all the green membranes were sintered first at 890 °C for as long as 2 hours by using a muffle furnace. This was done because the temperature increase in the provided high temperature furnace could not be controlled

when using a small rate of temperature increase. On the other hand, when using a muffle furnace, the rate of temperature increase could be set to $3\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. If the rate of temperature increase is too high, a thermal shock occurs in the BSCF membranes, hence causing the membranes to shatter/break apart during the process of sintering.

The double sintering process was done to produce membranes with high density. The relatively slow rate of temperature increase ($3\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$) was used to reduce the probability of forming residual stress as a result of a high rate of temperature increase, which in turn will cause the membranes to crack and eventually break apart [12].

The BSCF membranes before and after sintering at $1050\text{ }^{\circ}\text{C}$ and $1150\text{ }^{\circ}\text{C}$ are shown in Fig. 2. Based on these figures, it can be seen that all BSCF membranes experienced a significant shrinkage. But even so, the membranes produced were still intact, which is indicated by no signs of cracks and no traces of melting. The same results can also be found for BSCF membranes that were sintered at $1150\text{ }^{\circ}\text{C}$ as shown in Fig. 2c. However, the BSCF 7382 membranes that were produced were broken into two pieces.

Sintering at $1050\text{ }^{\circ}\text{C}$ was done by increasing the temperature directly from the room temperature up to the peak sintering temperature by using a high temperature furnace. The temperature increase in the high temperature furnace is very fast, where the temperature increased from a room temperature to $1050\text{ }^{\circ}\text{C}$ at a time period of in 30 minutes. Such sintering technique is called as non-phased sintering technique. The splitting of the BSCF 7382 membranes at sintering temperature of $1150\text{ }^{\circ}\text{C}$ was believed to take place because the membranes experienced a thermal shock as an effect of a very high rate of temperature increase of the furnace and due to a higher sintering temperature.

To avoid thermal shock, controlling the phased sintering technique was applied for the BSCF membranes that were sintered at $1150\text{ }^{\circ}\text{C}$. This stage of sintering is provided in Fig. 1 supplementary materials and is called phased sintering technique. The temperature of the high temperature furnace was maintained at a variety of temperatures ($450\text{ }^{\circ}\text{C}$, $650\text{ }^{\circ}\text{C}$ and $950\text{ }^{\circ}\text{C}$), each for as long as 1 hour before continuing up to $1150\text{ }^{\circ}\text{C}$. All membranes that were produced by the modified method of sintering are in intact forms which can be seen in Fig. 2d. This means that maintaining some of the temperatures to be below the final sintering temperature can reduce thermal shock and contributed a lot in maintaining the original shape of the sintered membranes.

The membranes produced were then tested for their density by using the water droplets method as reported by Utomo *et al.* [12]. Results of water droplet test can be found as Fig. 2 in the supporting materials to this article. The water droplets on the surface of the membranes, which were sintered at $1050\text{ }^{\circ}\text{C}$, were absorbed directly into the body of the membranes. This indicated that the membranes still had low density. On the contrary, the water droplets dripped on the surface of all the BSCF membranes, which were sintered at $1150\text{ }^{\circ}\text{C}$, lasted for more than 10 minutes. Hence it can be said that all three

of the membranes that were sintered at $1150\text{ }^{\circ}\text{C}$ are membranes with high density.

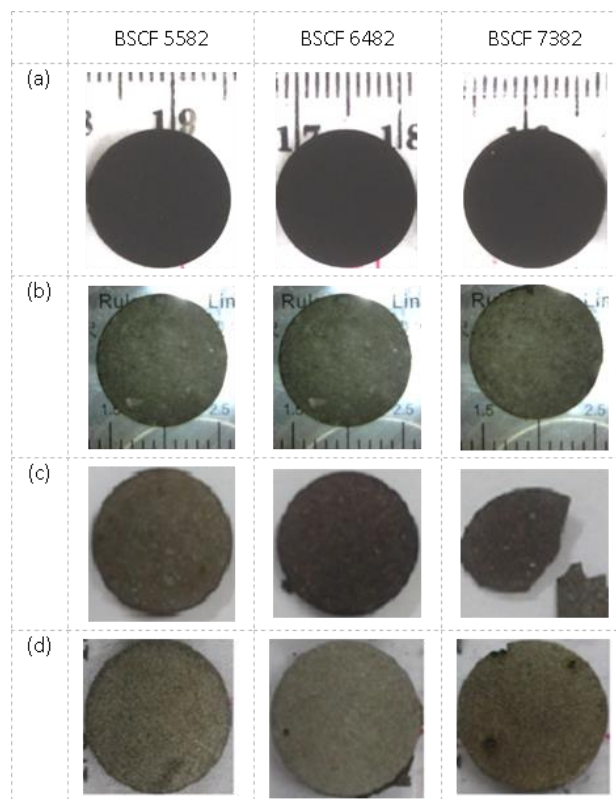


Fig. 2. BSCF membranes: (a) green membrane; (b) sintered at $1050\text{ }^{\circ}\text{C}$; (c) sintered at $1150\text{ }^{\circ}\text{C}$, and (d) after the phased sintering at $1150\text{ }^{\circ}\text{C}$.

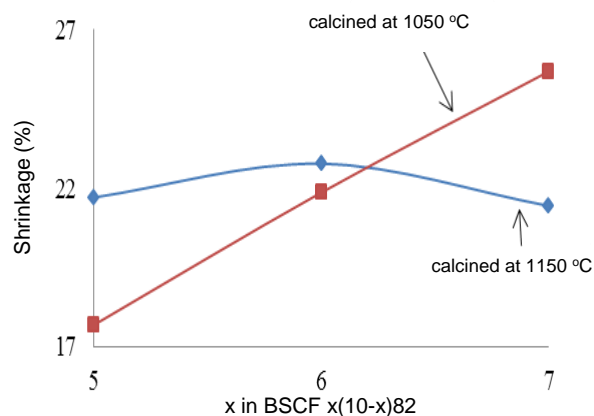


Fig. 3. The shrinkage pattern of the membranes after being sintered at $1050\text{ }^{\circ}\text{C}$ dan $1150\text{ }^{\circ}\text{C}$.

Even though efforts have been made to produce green membranes with very high density during the process of green membrane preparation, shrinkage on the sintered membranes could still happen. The measurement results of the shrinkage of the membranes can be seen in Fig. 3, which shows that the membranes that were sintered at $1050\text{ }^{\circ}\text{C}$ experienced an increase in the shrinkage as the amount of Ba^{2+} substituent increases. On the contrary, the membranes that were sintered at $1150\text{ }^{\circ}\text{C}$ experienced a decrease in the shrinkage. These opposite patterns that

took place may possibly be related to the microstructure of all the three membranes, all of which could be observed by SEM.

The SEM observation results on the surfaces of all the three sintered membranes at 1050 °C are shown in Fig. 4. Based on the three images shown in the figure, it can be seen that all membranes still have pores, which matches the results of the water droplets test. The pores experienced a decrease in the pore size as the amount of Ba²⁺ constituent increases. As reported by Utomo at al. [12], this phenomenon can be related to the existence of barium which has a lower melting point compared to strontium, and thus increasing the rate of particle growth as the amount of Ba²⁺ substituent increases.

But the pores that were seen were in a small amount. These pores can be seen in the BSCF 6482 and 7382 membranes that went through the process of non-phased sintering.

The non-phased sintering membranes that have rough surface could be caused by the abnormal particle growth, where the process of reorganizing the crystal structure of the membranes was not optimal, which caused the membranes to melt easily [11]. Traces of melting on the non-phased sintering membranes can be seen clearly as the amount of Ba²⁺ substituent increases. This type of melting was unexpected because this caused the shape of the membranes to be different from the expected membranes shape. Besides, this could also resist the diffusion rate of oxygen ion [13]. From the surface

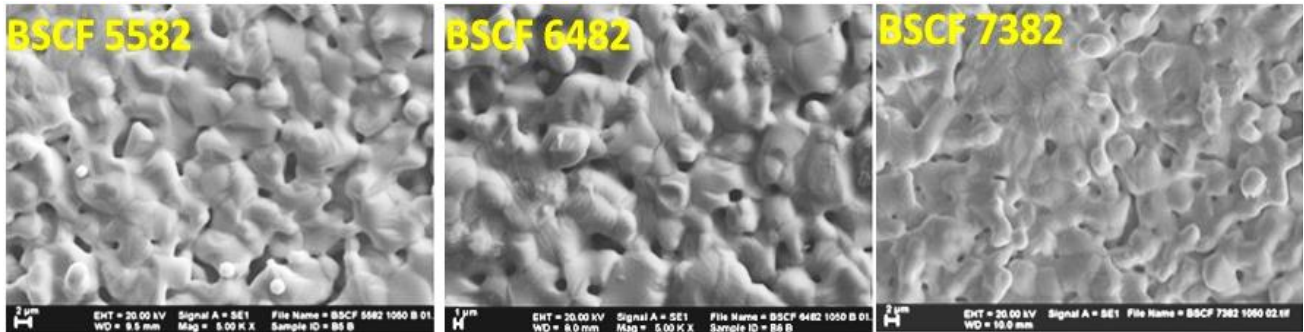


Fig. 4. Surface morphology of the membranes resulted from the non-phased sintering process at 1050 °C.

The morphology of all the three membranes that went through the process of sintering at 1150 °C can be seen in Fig. 5. The surface of the BSCF membranes was observed to be dense although a couple of pores can still be seen.

morphology explanation, it can be concluded that all the membranes that went through the process of phased sintering at 1150 °C are the membranes with the best high density.

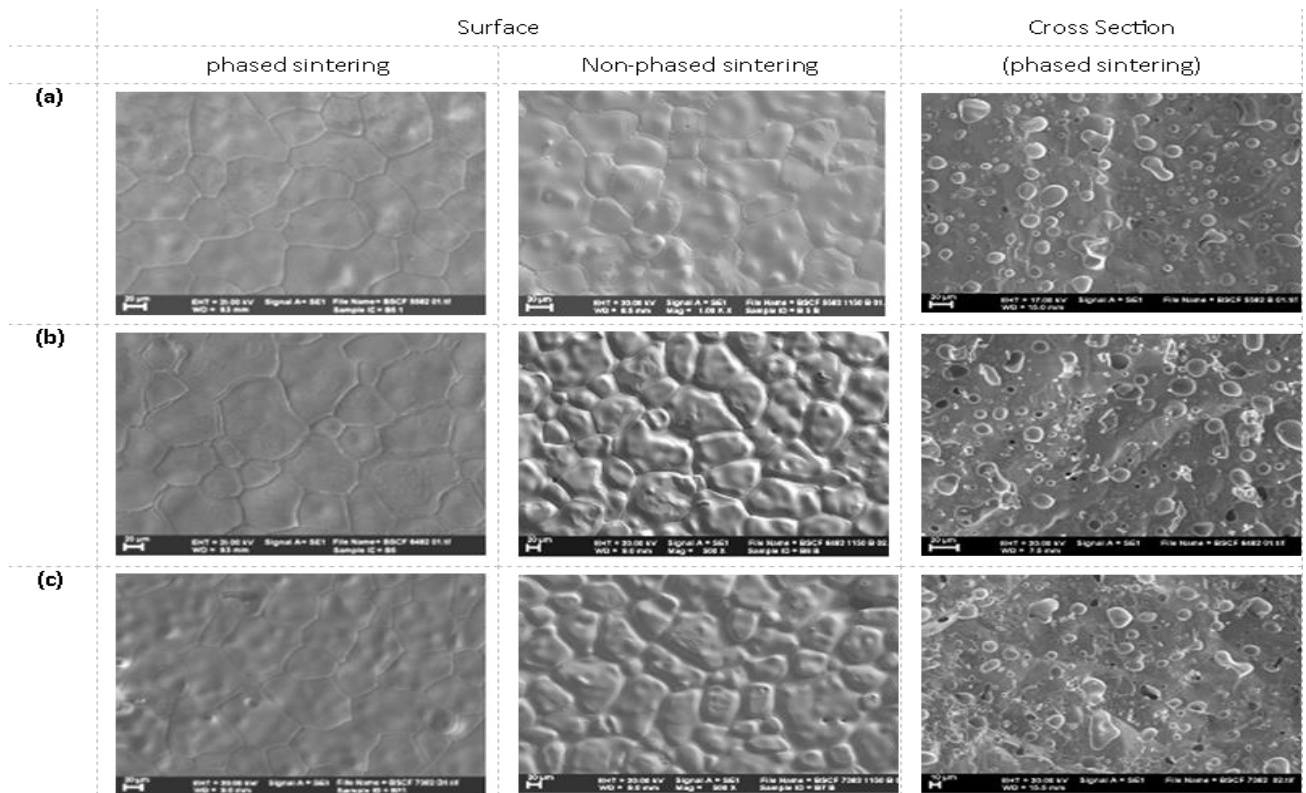


Fig. 5. Morphology of the surface and cross section of BSCF membranes after sintering at 1150 °C: (a) 5582, (b) 6482 (b) and (c) 7382.

The next stage was to observe the cross section of all the three membranes in order to find out the density on the cross section of the membranes. The SEM images of the cross section of the membranes can also be seen in **Fig. 5**. Based on the figure, it can be seen that pores exist on the interior of the BSCF membranes. However, the pores did not form a passage that went through from one side of the membrane to the other side which could be used for oxygen molecules to transfer.

The increase in the pore sizes could be resulted from two factors which are the membranes went soft and the BSCF membranes were reduced when they were sintered at 1150 °C. At 1150 °C, the perovskite oxides began to soften and at the same time the metal ions, which are cobalt and iron, began to reduce and release their oxygen lattice, turning them into oxygen gas. The oxygen gas then expanded and formed bubbles inside the membranes. The BSCF membranes with the higher amount of Ba²⁺ substituents are softer than the others, hence allowing the oxygen gas to expand at a greater amount which in turn forming bigger pores. A similar phenomenon had also been reported by Bauman and co-workers [15] which occurred to the BSCF 5582 membranes. The forming of the pores thus also explains the lower shrinkage value of the BSCF 7382 membranes compared to the BSCF 6482 membranes. The shrinkage of the BSCF 7382 membranes was reduced due to the formation of pores as explained previously.

The phenomena of the structure and the density of the membranes could have direct effects towards the hardness of the membranes. Basically, the membranes or the materials with a compacted structure (the atomic arrangements are closely packed, therefore forming strong atomic bonds) and a high density tend to have a high level of hardness and a low heat expansion [16]. In this case, all three membranes have stronger inter-atomic bond strength as the density on the inside of the membrane decreases. However, the effects of the strength of the atomic bonds towards the hardness and the heat expansion of the membranes are not yet known.

Therefore, the hardness and the heat expansion of all the three membranes needed to be analyzed further.

The hardness test results of the BSCF membranes are shown in **Table 1** which shows that the hardness value from the 5 points (position of the points can be found in the supporting information) are different from each other and the average level of hardness from the three membranes increased as the amount of Sr²⁺ increases. The difference in the hardness value from the similar membranes may be caused by the uneven distribution of the pores on the inside body of the membranes. On the other hand, the hardness value of the membranes which have the opposite effect as to the amount of Sr²⁺ constituents being added can be related to the pore size on the cross section of the membranes, where the pore size increased, the amount of Sr²⁺ substituents decreases. The other factor is the bonds between the arranging atoms of the membranes have effects on the hardness, where the smaller the amount of Sr²⁺ substituents used, the weaker the atomic bonds (as explained from the XRD results on the previous section), hence also resulting in a lower

hardness level. The hardness level of the three membranes that went through the process of phased sintering at 1150 °C are (measured in HV/Hardness Vickers), from the weakest to the strongest, BSCF 5582 > BSCF 6482 > BSCF 7382.

Table 1. The hardness of the BSCF 5582, 6482, and 7382 membranes after phased sintering at 1150 °C

No. of indentation point	Hardness (HV)		
	BSCF 5582	BSCF 6482	BSCF 7382
1	413.90	441.00	390.00
2	465.80	469.00	438.50
3	448.40	434.00	433.50
4	368.50	426.60	343.00
5	523.60	381.40	470.60
Average	444.04	430.40	415.12

The thermal expansion characteristics of the three 1150 °C phased sintering membranes were tested by using the TMA in air with the applied load of 0,02 N. The test results show that all three of the membranes experienced an increase in thermal expansion as the temperature increases (**Fig. 6**). The pattern can be related to the increasing distance between the bonds of the metal-oxygen ions which is also followed by the increase in cell volume.

Besides experiencing thermal expansion, all membranes also experienced a chemical expansion as reported by Tai et al. [16] when they studied the La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} membrane. The chemical expansion took place at the same time during which the thermal expansion occurred, hence this is why the graph in **Fig. 6** shows clearly a drastic increase of expansion during the temperatures of 550-700 °C. Due to the chemical expansion, the thermal expansion pattern produced did not follow the amount of Sr²⁺ substituents anymore.

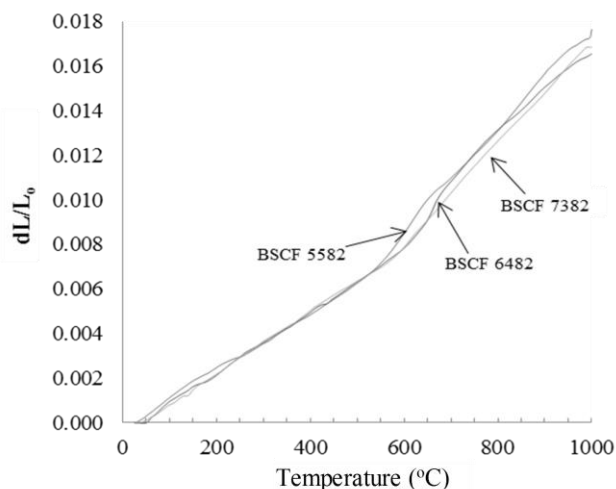


Fig. 6. The heat expansion pattern of the BSCF 5582, 6482 and 7382 membranes.

The increase in thermal expansion as the amount of Ba²⁺ substituents increased can be seen at the temperature

range between 25 °C and 450 °C. Even so, the difference is so small among membranes. At temperatures of above 450 °C, the order of the expansion degrees of the BSCF membranes is no longer proportional to the order of the increasing amount of the Ba²⁺ substituents. The BSCF membranes have different degrees/order of thermal expansion at every different range of temperatures.

Based on the explanation given by Huang and co-workers [17], there are two possibilities that could lead to a change in the expansion pattern which are: (i) the existence of the repelling forces between the neighboring cations as an effect of oxygen lattice discharge and (ii) a spontaneous reduction took place on site B (on the cobalt and metal ions) to balance the process of forming oxygen lattice vacancy. When reduced, the radius of the cobalt and metal ions increases. The radius of the ions Co⁴⁺, Co³⁺, Co²⁺, Fe⁴⁺, and Fe³⁺ in respective order are 0.530; 0.610; 0.745; 0.585; dan 0.645 Å [18]. The reduction of Co⁴⁺ and Fe⁴⁺ to Co³⁺ and Fe³⁺ could take place at 400 °C to 600 °C and the reduction of Co³⁺ to Co²⁺ could take place at temperatures of 750 °C to 1000 °C as reported by Babakhani and co-workers [4]. Thus this explains why all of the membranes showed a drastic expansion change at these range of temperatures. The results of the thermal expansion coefficient of the BSCF membranes match with the morphology observations of the cross section of the membranes which had been explained previously.

When observed from the average expansion coefficient at 25 °C to 1000 °C, the order of the thermal expansion coefficient of the three membranes are BSCF 5582 > BSCF 6482 > BSCF 7382, as shown in **Table 2**. The higher the amount of Ba²⁺ substituents used, the smaller the average thermal expansion coefficient of the membranes. This pattern is very similar to the oxygen desorption pattern of the BSCF 5582 and BSCF 7382 membranes, which had been reported by Babakhani and co-workers [4], which stated that the oxygen desorption of the BSCF 5582 membrane is larger than the oxygen desorption of the BSCF 7382 membrane at temperatures of 25 °C to 100 °C. Hence, the BSCF 7382 is a membrane with the best thermal stability when compared to BSCF 6482 and 5582 membranes.

Table 2. The average TEC (Thermal Expansion Coefficient) values of the BSCF 5582, 6482, and 7382 membranes.

Temperature (°C)	TEC (ppm.°C ⁻¹)		
	BSCF 5582	BSCF 6482	BSCF 7382
25-450	12.64	13.58	14.00
450-700	23.75	20.64	18.71
700-800	21.13	23.33	23.27
800-900	25.87	19.11	21.19
900-1000	17.60	15.47	22.32
25-1000	18.28	17.75	17.49

Conclusion

The perovskite oxides of BSCF 5582, BSCF 6482 and BSCF 7382 were successfully synthesized by solid state method. The oxides had a cubic structure with a high level of purity. High density BSCF membranes were obtained by using the phased sintering technique at a final

sintering temperature of 1150 °C. The existence of Ba²⁺ on the BSCF membranes affects their mechanical properties which include density, hardness and thermal expansion coefficient. Membranes that were sintered at 1150 °C have dense surfaces and the density on the cross section of the membranes increased as the amount of Ba²⁺ increases. The same pattern was also found on the hardness and the thermal expansion coefficient of the membranes. As the amount of Ba²⁺ substituent increases, the hardness of the BSCF membranes decreased and so does their thermal expansion coefficient. Appropriate conclusion needs to be written here which reflects the exact finding demonstrated in the paper.

Acknowledgements

The authors would like to thank the Ministry of Research, Technology and Higher Education of the Republic of Indonesia who funded this research through research scheme of “Strategis Nasional” in financial years of 2014-2016.

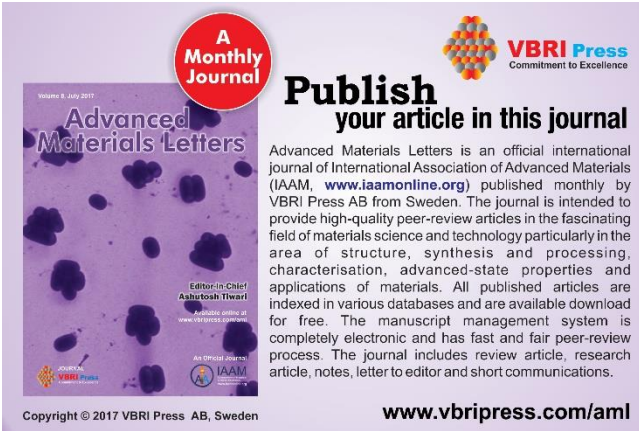
Author's contributions

Conceived the plan: HF, WPU, DP, NW; Performed the experiments: MIS, SR, ADM; Data analysis: HF, WPU, IKM, S; Wrote the paper: HF, WPU, S. Authors have no competing financial interests.

References

- Ishihara, T.; Tsuruta, Y.; Todaka, T.; Nishiguchi, H.; Takita, Y; *Solid State Ionics*, **2001**, *152*, 709.
DOI: [10.1016/S0167-2738\(02\)00413-7](https://doi.org/10.1016/S0167-2738(02)00413-7)
- Tan, X.; Wang, Z.; Liu, H.; Liu, S; *J. Membrane Sci.*, **2008**, *324*, 128.
DOI: [10.1016/j.memsci.2008.07.008](https://doi.org/10.1016/j.memsci.2008.07.008)
- Yang, W.; Wang, H.; Zhu, X.; Lin, L; *Top. Catal.*, **2005**, *35*, 155.
DOI: [10.1007/s11244-005-3820-6](https://doi.org/10.1007/s11244-005-3820-6)
- Babakhani, E.G.; Towfighi, J.; Shirazi, L.; Pour, A.N; *J. Membrane Sci.*, **2011**, *376*, 78.
DOI: [10.1016/j.memsci.2011.04.004](https://doi.org/10.1016/j.memsci.2011.04.004)
- Huang, B.X.; Malzbender, J.; Steinbrech, R.W.; Singheiser, L; *Solid State Ionics*, **2009**, *180*, 241.
DOI: [10.1016/j.ssi.2008.11.005](https://doi.org/10.1016/j.ssi.2008.11.005)
- Shao, Z.; Xiong, G.; Tong, J.; Dong, H.; Yang, W; *Sep. Purif. Technol.*, **2001**, *25*, 419.
DOI: [10.1016/S1383-5866\(01\)00071-5](https://doi.org/10.1016/S1383-5866(01)00071-5)
- Chanda, A.; Huang, B.X.; Malzbender, J.; Steinbrech, R.W; *J. Eur. Ceram. Soc.*, **2011**, *31*, 401.
DOI: [10.1016/j.jeurceramsoc.2010.10.022](https://doi.org/10.1016/j.jeurceramsoc.2010.10.022)
- Patra, H.; Rout, S.K.; Pratihari, S.K.; Bhattacharya, S; *Int. J. Hydrogen Energy*, **2011**, *36*, 11904.
DOI: [10.1016/j.ijhydene.2011.06.021](https://doi.org/10.1016/j.ijhydene.2011.06.021)
- Bonturim, E.; Vargas, R.A.; Andreoli, M.; Satoshi, E.; Seo, E.S.M; *Materials Science Forum*, **2012**, *764-768*
DOI: [10.4028/www.scientific.net/MSF.727-728.764](https://doi.org/10.4028/www.scientific.net/MSF.727-728.764)
- Kong, L.B.; Zhang, T.S.; Ma, J.; Boey, F; *Prog. Mater Sci.*, **2008**, *53*, 207.
DOI: [10.1016/j.pmatsci.2007.05.001](https://doi.org/10.1016/j.pmatsci.2007.05.001)
- Das, N.; Maiti, H.S; *J. Eur. Ceram. Soc.*, **1999**, *19*, 341.
DOI: [10.1016/S0955-2219\(98\)00205-2](https://doi.org/10.1016/S0955-2219(98)00205-2)
- Utomo, W.P.; Aliyatulmuna, A.; Fansuri, H; Research Session 3: Chemistry, 8th *International Student Conference on Advanced Science and Technology (ICAST)*, Kumamoto, Japan, **2014**.
- Tan, L.; Gu, X.; Yang, L.; Jin, W.; Zhang, L.; Xu, N; *J. Membrane Sci.*, **2003**, *212*, 157.
DOI: [10.1016/S0376-7388\(02\)00494-5](https://doi.org/10.1016/S0376-7388(02)00494-5)
- Xu, N.; Zhao, H.; Zhou, X.; Wei, W.; Lu, X.; Ding, W.; Li, F; *Int. J. Hydrogen Energy*, **2010**, *35*, 7295.
DOI: [10.1016/j.ijhydene.2010.04.149](https://doi.org/10.1016/j.ijhydene.2010.04.149)
- Baumann, S.; Schulze-Küppers, F.; Roitsch, S.; Betz, M.; Zwick, M.; Pfaff, E.M.; Meulenberg, W.A.; Mayer, J.; Stöver, D; *J. Membrane Sci.*, **2010**, *359*, 102.
DOI: [10.1016/j.memsci.2010.02.002](https://doi.org/10.1016/j.memsci.2010.02.002)

16. Tai, L.-W.; Nasrallah, M.M.; Anderson, H.U.; Sparlin, D.M.; Sehlin, S.R; *Solid State Ionics*, **1995**, 76, 259.
DOI: [10.1016/0167-2738\(94\)00244-M](https://doi.org/10.1016/0167-2738(94)00244-M)
17. Huang, B.X.; Malzbender, J.; Steinbrech, R.W.; Wessel, E.; Penkalla, H.J.; Singheiser, L; *J. Membrane Sci.*, **2010**, 349, 183.
DOI: [10.1016/j.memsci.2009.11.047](https://doi.org/10.1016/j.memsci.2009.11.047)
18. Shanon, R.D; *Acta Crystallogr., Sect. A: Found. Crystallogr.*, **1976**, 32, 751.
DOI: [10.1107/S0567739476001551](https://doi.org/10.1107/S0567739476001551)



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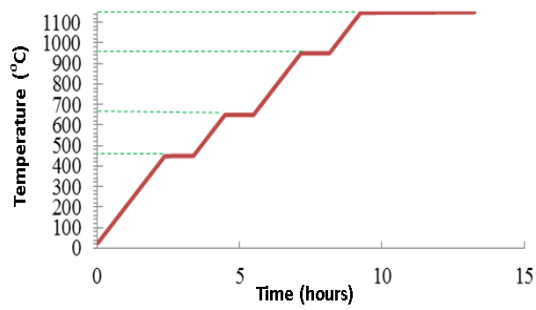


Fig. 1. Temperature program of phased sintering at 1150 °C

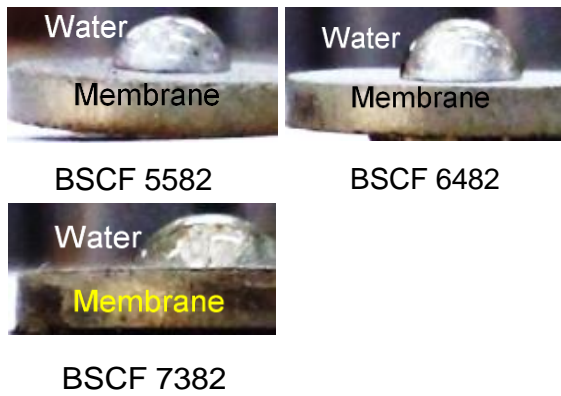


Fig. 2. Water droplets test results on the surface of the BSCF membranes after phased sintering at 1150 °C.

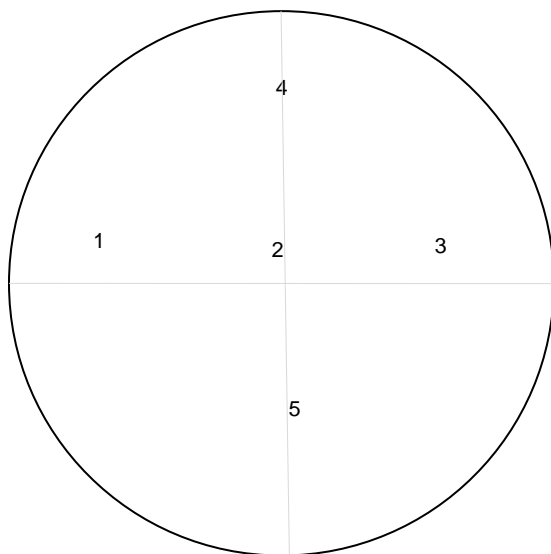


Fig. 3. Indentation points on the surface of the BSCF 5582, 6482, and 7382 membranes