Crystal structure analysis of double perovskite (Bi, Sr)(Co, Fe)O$_{6-\delta}$ for intermediate temperature solid oxide fuel cells (IT-SOFCs): A preliminary study

Arham$^1$, D Tahir$^1$, F Destyorini$^2$, A Hardiansyah$^2$, N Indayaningsih$^2$, D S Khaerudini$^{2,*}$

$^1$Department of Physics, Hasanuddin University, Jl. Perintis Kemerdekaan KM 10, Makassar, South Sulawesi, Indonesia
$^2$Research Center for Physics, Indonesian Institute of Sciences (LIPI), Bld. 440-442 Kawasan Puspiptek Serpong South Tangerang 15314, Banten, Indonesia

*E-mail: deni.shidqi.khaerudini@lipi.go.id

Abstract. Double perovskite-type Bi$_x$Sr$_{2-x}$Co$_{0.5}$Fe$_{1.5}$O$_{6-\delta}$ (BiSCF) oxides with various A-site ($x = 0.6, 0.7, 0.8$, designated as BiSCF06, BiSCF07, BiSCF08, respectively) have been synthesized by a solid-state reaction technique, and investigated on their structure properties of perovskite powder for application of intermediate-temperature solid oxide fuel cells (IT-SOFCs) purpose with related to the calcination temperatures at 950, 1000 and 1050°C. The crystal structure of the BiSCF powder was analyzed by X-ray diffractometer (XRD), and determined by Rietveld refinement. The results show that BiSCF07 powder which calcined at 950°C shows the best structure of cubic perovskite with space group $Pm-\bar{3}m$ and a lowest impurity at room temperature indicated structure stability and offers a higher mobility of oxygen vacancies. Based on this result, BiSCF07 powder has a potential to be developed as cathode for IT-SOFCs applications.

1. Introduction

Recently, perovskite becomes an attractive material due to its widely properties. Theoretically, perovskite structure has general formula of $ABX_3$. Specifically, the family of perovskite oxides ($ABO_3$, known also as single perovskite, for double perovskite is $AA'B'B'O_6$) are possibly the best oxide structure due to its great stability of physical and chemical properties [1]. Further, perovskite oxide have been developed for widely application such as oxygen separation, oxygen transporting membranes, aluminium air batteries cathode, as well as including in oxygen sensor, catalyst and electrode in SOFCs applications [2-6].

SOFCs are one important energy conversion devices which can directly produce electricity by electrochemical process [7-9]. Being energy conversion, SOFCs have many advantages among power generation technologies, such as energy efficiency exceedingly high up to 85% [7]; greenhouse gas emission is much lower than any other conventional power plants, and comprehensive fuel flexibility [9-13]. Since SOFCs operated at high temperature as high as 1000°C, it causes several problems such as degradation, interface reaction, fabrication cost and also tough to be commercialized [14-16]. Being defiance to prolong the lifetime of SOFCs components, reducing fabrication cost and improving the
performance device for large scale application are still remain challenge to be developed. Improvement cathode material which has high stability and electrocatalytic performance at reduced temperature plays a key role for development of IT-SOFCs. The ideal cathode (oxygen electrode material) has many requirements, such as high mixed ionic electronic conductivity (MIEC), excellent chemical and thermal stability between cathode and electrolyte, large amount of triple phase boundary (TPB of oxygen-cathode-electrolyte) and high catalytic activity [17, 18].

In the past decade, double perovskite materials have attracted much interest due to their high catalytic activity, conductivity and magnetic properties [9, 19-21]. Generally, cobalt based double perovskite MIEC presented higher catalytic activity and offer a large amount of oxygen vacancies [8]. From the various material, Sr₂+ have much attracted because of their excellent properties including their low thermal expansion coefficient, highly chemical stability and advantageous electrocatalytic activity for oxygen reduction reaction (ORR) [22]. Wedig et al. [23] and Khaerudini et al. [21] found that the presence of Bi³⁺ ion ([Xe] 4f¹⁴5d¹⁰6s²6p⁰) on the A site of their single perovskite; thus it made cathode more polarizable due to its 6s lone pair and increase the structural stability. Moreover, the introduction of A-site non-stoichiometry (A-A’ deficiency) into the lattice structure of crystal of double perovskite oxide forced weighty effect on the thermal, electrochemical, electrical properties [17, 21, 23-24].

Therefore, the advantage of the double perovskite structure will be elaborated more in this. The objective of this present study is to develop a novel double perovskite materials in stoichiometric structure of (Bi, Sr₂-x)(Co₂-xFe₁-x)O₃, with the major focus on the effect of A-site deficiency on their structure properties with respect to the calcination temperature. It is supposed to find a novel cathode material for IT-SOFCs application.

2. Experimental Methods

2.1 Sample preparations
The original powder of BiSCF (BiₓSr₂-xCo₂-xFe₁-xO₃) oxides with initial x = 0.6, 0.7, 0.8, designated as BiSCF06, BiSCF07 and BiSCF08, respectively, are developed. The powders were prepared by wet-solid state reaction method by high-purity reagent of Bi(NO₃)₃.5H₂O (Kanto Chemical, Japan 99.5%), Sr(NO₃)₂, Co(NO₃)₂.6H₂O (Kanto Chemical, Japan 98%) and Fe(NO₃)₃.9H₂O (Merck, Germany 99.5%) materials. The stoichiometric amount of these powders thoroughly mixed and ball milled for 7 hours using zirconium balls and jar zirconia as grinding media with ball to powder ratio 5:1 wt.%. The milling was conducted in air at room temperature at a rotational speed of 325 rpm in methanol medium to obtain homogenize powder. The resulting mixture was oven-dried at 80-120°C for 24 h and thoroughly ground in agate mortar and calcined at 950, 1000 and 1050°C for 8 h in air, with a heating rate of 3°C/min to obtain a single phase of BiSCF powders.

2.2 Material characterizations
The phase purity and lattice structure of the samples were examined at room temperature by powder XRD (Rigaku SmartLab) using Cu-Kα (λ = 1.541862 Å) radiation source over the angular range of 10 ≤ 2θ ≤ 90°. The scanning was collected at a step width of 0.01°. Rietveld refinement was performed by using High Score Plus™ [25] in order to determine space groups and lattice constant of developed BiSCF powders.

3. Results and Discussion
The XRD analysis was performed to identify perovskite phase of the various developed powders (BiSCF06, BiSCF07 and BiSCF08). In this work, BiSCF powder was synthesized by solid state reaction method. The room temperature of XRD patterns of all developed powders (BiSCF06, BiSCF07 and BiSCF08) have been analyzed and shown in figure 1 after calcined at 950, 1000 and 1050°C for 8 hours in air.
Figure 1. Room temperature XRD profile of (a) BiSCF06, (b) BiSCF07 and (c) BiSCF08 powders after calcination at 950 °C, 1000 °C and 1050 °C for 8 h in air, respectively.
The results display that the pattern of BiSCF powders indicated perovskite phase with impurities occur at each temperature for all composition (BiSCF06, BiSCF07 and BiSCF08). However, the BiSCF07 shows perovskite phase with less impurity at 950 °C among the powders. When the calcination temperature increases, more impurity phases are found at 1000 and 1050°C, respectively. Therefore, T = 950 °C is fixed as the optimum calcination temperature for the preparation of double perovskite BiSCF07 powder in this research.

The crystal structure information has been calculated by refinement analysis. From Rietveld refinement of BiSCF07, the R factor values can be determined by using High Score Plus software (R_p = 8.862, R_wp = 11.149 and R_exp = 9.796 and \( \chi^2 = 1.295 \)). The chi square (\( \chi^2 \)) propose the (R_wp/R_exp)² factors and it shows the goodness of fit between experimental data and model [26]. This result displays good fitting between experimental data and model. The refined lattice parameters including their R factors and \( \chi^2 \) of all developed powders BiSCF (x = 0.6, 0.7, 0.8) are listed in table 1. The pattern of BiSCF07 is resulted on cubic unit cell with space group of Pm-3m. The calculated lattice parameter is 3.9343 Å with cell volume of 60.89791 Å³.

Figure 3 shows Bi\(_2\)Sr\(_2\)Co\(_3\)Fe\(_{1-x}\)O\(_{6-\delta}\) pattern and the lattice expansion of all powder at 950 °C magnified at around 2\( \theta \) = 32°, with x = 0.6, 0.7 and 0.8, respectively. It is clearly that the main peak is shift continuously to the lower 2\( \theta \). The lattice parameters increase when Sr-deficient increase from 0.6 to 0.7. However, if the x values increase to 0.8, lattice parameter is decreased but still higher than x = 0.6 followed by volume expansion 60.55493, 60.89791 and 60.64287 Å³ (x = 0.6, 0.7, 0.8), respectively. The result suggests that BiSCF07 is the maximum expansion of the lattice volume. However, all of the pattern show lattice expansion trend.

![Figure 2](image-url) Rietveld refinement of BiSCFF07 after calcination at 950°C for 8 hours in air. The red line represent calculated diffraction, the black thick line shows observation pattern and the last blue line represent difference between calculation and observation data.

| Sample  | Space group | \( a \) (Å) | \( V_{\text{calculation}} \) (Å³) | \( V_{\text{theoretical}} \) (Å³) | \( \rho_{\text{theoretical}} \) (gr cm⁻³) | \( R_p \) | \( R_{wp} \) | \( R_{exp} \) | \( \chi^2 \) |
|---------|-------------|-------------|-----------------|-----------------|------------------|-------|-------|-------|-------|
| BiSCF06 | Pm-3m       | 3.9269      | 60.55493        | 60.73867        | 8.97333          | 8.769 | 11.214| 9.190 | 1.489 |
| BiSCF07 | Pm-3m       | 3.9343      | 60.89791        | 61.08269        | 8.92016          | 8.862 | 11.149| 9.796 | 1.295 |
| BiSCF08 | Pm-3m       | 3.9288      | 60.64287        | 60.82688        | 8.95767          | 9.572 | 12.312| 9.856 | 1.561 |
Figure 3. Refined X-ray diffraction for BiSCF06, BiSCF07 and BiSCF08 powders after calcination at 950 °C for 8 hours in air. On the right side: magnification around 2θ= 32°.

Theoretical densities and the comparisons between calculated and theoretical lattice volume for all of BiSCF powders (BiSCF06, BiSCF07 and BiSCF08) are also listed in table 1, respectively. The calculated lattice volume is differing from theoretical values by lower than 1%. So this result shows good agreement between observation and theoretical volume. From table 1, the results show that the theoretical densities is inversely proportional to the lattice volumes which represent that the volume expansion is consequently increasing the distance all of atom in the lattice.

4. Conclusions
The structure of double perovskite BiSCF oxides were synthesized by a solid state reaction method was successfully analyzed. The powder prepared with various x = 0.6, 0.7 and 0.8, designated as BiSCF06, BiSCF07 and BiSCF08 and calcined at 950, 1000 and 1050 °C for 8 hours in air. From XRD analysis, the lowest impurity phase of BiSCF double perovskite with cubic structure was formed by calcining 950 °C with x = 0.7 (Bi:Sn1.3Co0.5Fe1.5O6-δ). Therefore, the BiSCF07 powder which calcined at 950 °C shows the best perovskite phase among the prepared powders.

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