Structure refinement of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$ as cathode materials for intermediate temperature solid oxide fuel cells (IT-SOFC)

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Abstract. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was successfully prepared using modified solid-state synthesis routes. The lowest temperature to obtained single phase of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ is about 900ºC for 15 hours. Longer period of time are required compared to only 5 hours at 950ºC as established in literatures. The X-ray Diffraction (XRD) data confirmed that $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ is formed a cubic perovskite with the space group of Pm-3m. The lattice parameters of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ are a = 3.990 (1) Å and unit cell volume is V = 63.5 (1) Å^3. The Rietveld refinement of XRD data revealed that the crystal structure of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ slightly changes as a function of temperature.

INTRODUCTION

Oxide ion conductors based on perovskite-type structure has attracted a significant attention due to their great properties of mixed ionic and electronic conductivity (MIEC). Its' mainly developed to be utilised as a cathode for the solid oxide fuel cells (SOFCs) [1]. For example, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was reported as a potential cathode materials for intermediate temperature solid oxide fuel cell (IT-SOFC) [2]. It had possess high oxygen permeation flux that were leads to high concentration of oxygen vacancies at the temperature range between 600 and 800 ºC compared to $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ [3].

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ is an oxide ion conductor that formed with perovskite structure. It is isostructure with the $SrCo_{0.8}Fe_{0.2}O_3$. Furthermore, it has a cubic symmetry at room temperature with the space group of Pm-3m. This cubic symmetry of perovskite remain stable in wide range of temperature even in reducing atmosphere up 900°C [5].

In this paper, we were reported crystal structure analyses of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ that were prepared between 900 and 1100ºC in air. Our aim is to help further understanding on their crystallographic properties that underpinned their properties as the oxide ion conductors.

EXPERIMENTAL

The starting materials that were used are barium nitrate (98%), strontium nitrate (98%), cobalt (II) nitrate hexahydrate (98%) and iron (III) nitrate nonahydrate (98%), ethylene diamine tetra-acetic acid (EDTA), $C_{10}H_{16}N_2O_8$ (98%), ammonium hydroxyl solution, NH_4OH and citric acid monohydrate, (98%), $C_6H_8O_7.H_2O$. Initially, a buffer solution of EDTA-NH_3OH was prepared by dissolving EDTA into 50 ml of NH_3OH. The mixture was stirred in a 500 ml beaker until a clear solution obtained. Then, a stoichiometric amount of $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Co(NO_3)_2$ and $Fe(NO_3)_3$ were weighted and added into the EDTA-NH_3OH buffer solution. The solution was stirred continuously to ensure all metal nitrates were dissolved in the solution.

After that, an appropriate amount of citric acid was added with ratio to metal nitrates and EDTA content of 1.5:1:1. EDTA and citric acid were used as a chelating agent for the complex nitrate salts to avoid problematic formation of secondary phase. On the other hand, the pH solution was controlled to about 6 by adding NH_4OH into the solution.

Furthermore, the solution was heated on a hotplate at 90°C for a few hours until it became a gel (gelation process completed). The gel was heated in oven up to 250°C and then remained for 5 hours before it cooled to room temperature. The fired product was removed from the beaker and then ground using pestle and mortar. After that, the obtained powder was fired between 900 and 1100°C with intermittence grindings.

The purity of products was analysed using X-ray powder diffraction (XRD) Brukers D2 Phaser with Cu-Kα that equipped with LYNXEYE 1-D ultra-fast detector at 30 kV and 10 mA, respectively. All scans were performed between $2\theta = 20°$ and 70° with 0.02 step size. All the phase pure samples were then scanned for a longer duration of time to obtain minimum intensity of 10,000 for Rietveld refinement analysis. The Rietveld refinement was performed using GSAS/EXPEGUI software to determine structural parameter and crystallographic properties of the prepared samples [6].

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for sample that was heated at 900°C for 5, 10 and 15 hours. The sample was not fully reacted yet after heated for 5 hours. Then, the sharp and well-defined reflections could be observed after 10 hours. However, two small reflections of unknown impurities were observed at $2\theta = 27.43°$ and 42.62°. Furthermore, all the reflections that belong to impurity phase were disappeared after 15 hours at 900°C. Thus, it resulting only reflections that belong of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was remained.

The result shows that a cubic perovskite of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ with the space group of Pm-3m was obtained after sample was prepared at 900°C for 15 hours. It is well established in literatures that the optimum synthesis temperature for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was at 950°C and 1000°C for 10 and 5 hours, respectively [6,7]. Thus, it is indicated that the cubic phase of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ could be obtained as low as 900°C using modified solid synthesis route. It is quite reasonable for any solid-state synthesis method that lower reaction temperature requires slightly a longer period of time to complete their reaction.

Figure 2 shows the comparison of XRD patterns for samples that prepared between 950 and 1100°C for 5 hours except for 900°C for 15 hours. The reflections are quite similar for all samples from 900 to 1100°C. The reflection of (110) is remaining unchanged as the strongest Bragg's reflection as a function of temperature. Thus, it is a clear indicator that the cubic phase of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ is quite stable up to 1100°C.
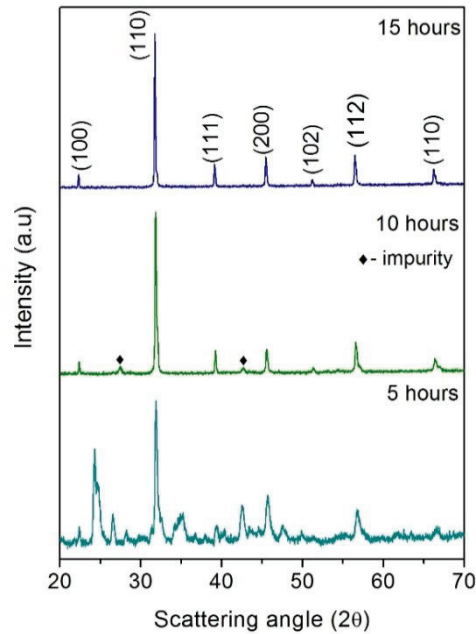
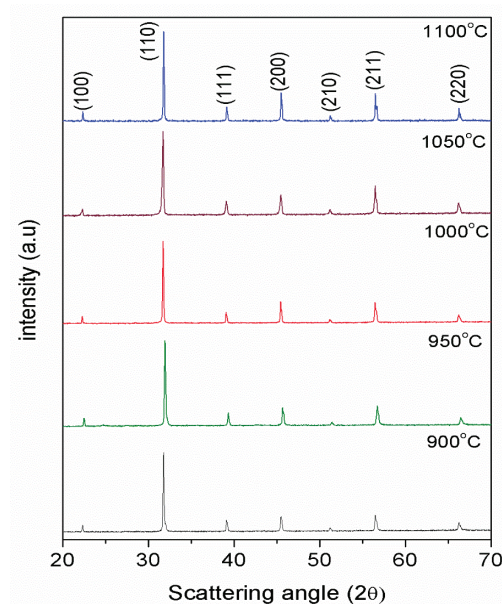**FIGURE 1.** The XRD patterns of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ that heated at 900°C between 5 and 15 hours.

FIGURE 2. The XRD pattern of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ that heated between 900 and 1100°C in air.

Figure 3 shows the lattice parameter and unit cell volume of the indexed XRD patterns obtained using least-square refinement are a =. The results showed that the lattice parameter of the cubic phase $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ remain similar within error for sample that heated at 900ºC and 950ºC. Then, the lattice parameters are gradually increased from 950 to 1050ºC. However, the lattice parameters suddenly reduced in the sample that heated at 1100ºC. Thus, it resulting unit cell volume gradually expanded as temperature increased from 950 to 1050ºC. But, the unit cell volume was suddenly shrunk at 1100ºC.
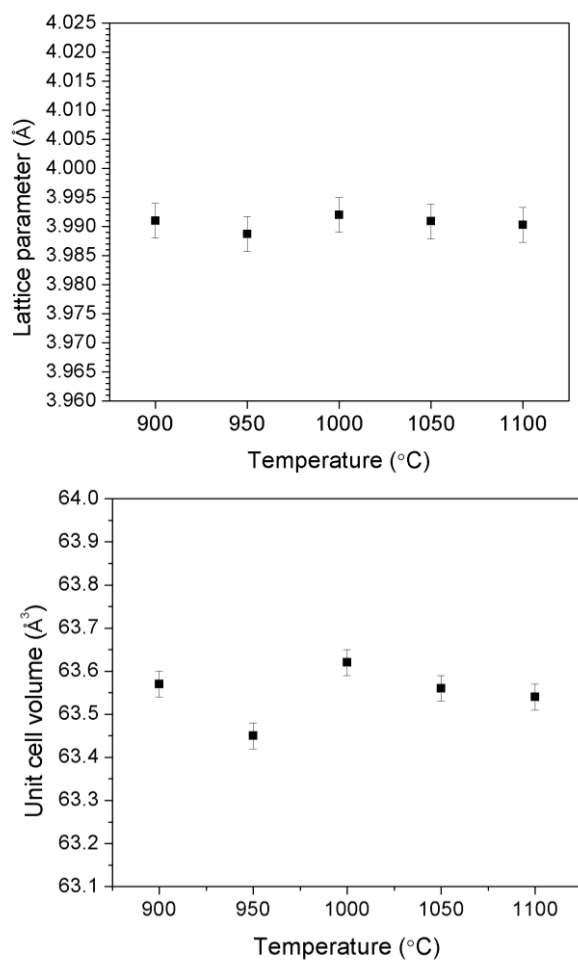
FIGURE 3. Lattice parameter and unit cell volume of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ that heated between 900 and 1100°C.

The changes in lattice parameters and unit cell volume as a function of temperature could give an indicator about the temperature stability of sample at high temperature. The sample was remained stable up to 950°C. Then, the expansion of lattice parameters and unit cell volume at above than 950°C probably due to oxygen loss or oxygen deficiency might occur in the sample. When oxygen anions are start losing from the lattice, the transition metal element(s) that occurred in the composition will be oxidised to remain their electroneutrality. Although, the oxidation of transition metal element(s) in the composition may be the best assumption so far to describe changes in the lattice parameters and unit cell volume, it merely speculation since the conventional XRD is not sensitive to determine the occupancy of oxygen in the lattice.

Rietveld Revinement

The Rietveld refinements were carried out by using the XRD data to evaluate the structural changes if possible on the crystal structure of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ as a function of temperature. The initial structure model was selected from the ICSD database for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (ICSD No.:109462) as shown in Table 1. The initial values for lattice parameters were taken from the least-square refinement as shown in Figure 3. The instrument parameter file for the XRD D2 Phaser was prepared by using Corundum standard. The default values for thermal parameter (Uiso) were used in all subsequence refinements.

TABLE 1. The initial structure model of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (ICSD No: 109462)

Atom	Wyckoff Position	Atomic position (x,y,z)	Occupancy	Thermal parameter (U_{iso} x 100) (Å^2)
Ba	1a	0,0,0	0.5	0.025
Sr	1a	0,0,0	0.5	0.025
Co	1b	½,½,½	0.8	0.025
Fe	1b	½, ½, ½	0.2	0.025
O	3c	½,½,0	1.0	0.025

Type of crystal	Cubic
Space group	Pm-3m
Lattice parameter	a = 3.9873(1) Å
& unit cell volume	V = 63.39 (1) Å^3

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ has formed as a perovskite-type structure with the formula of ABX_3 and the space group of Pm-3m. A and B is referred to cation whereas X is an anion. A-site always referred to cation that has relative bigger size and located at the edge of the unit cell (0,0,0). Meanwhile, B-site always referred to the cation that has relatively smaller size and located at the centre of the unit cell (½,½,½). Thus, Ba and Sr are sharing at the A-site (0,0,0) while Co and Fe are sharing at the B-site (**½,½,½**) in the lattice. Furthermore, Ba and Sr have 12 coordination numbers whereas Co and Fe located at the octahedral site that surrounded with six oxygen ions.

Table 2 shows the refined structural model for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ that prepared at different temperature. The XRD data were analysed using Rietveld refinement based on the initial structural model as shown in Table 1. Results show that the disagreement between calculated and observed patterns are consider very low with the value of R_{wp} and R_p were less than 10% except the sample that prepared at 1050°C. Furthermore, the χ^2 are about 1.2 except for 1050ºC.

Figure 4 shows the patterns fit of refined structure model obtained from Rietveld refinements. The patterns fit was plotted as observed (red), calculated (green) and differences plot (purple). Results show that the calculated and observed patterns are almost fitted and matched. Thus, we are believed that the crystal structure of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ could represent by the refined structural model as shown in Table 2.

Figure 5 shows the atomic simulation of the refined structural model of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$. The green balls represent Ba and Sr atoms that are located at the edge of unit cell. While, the red balls that placed on each face of unit cell are represent O atoms. Furthermore, the blue balls that are located at the centre of unit cell represent Co and Fe atoms. The Ba/Sr on the A-site have 12-fold coordination while Co/Fe on the B-site have 6-fold coordination in the square pyramids of O anions. The structure quite stable as the square pyramids form corner sharing between other square pyramids of $(Co, Fe)-O_6$. Hence, this is the reason why cubic phase of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ maintain when heated from 900 to 1100°C

TABLE 2. Refinement structural model for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ that prepared between 900 and 1100°C

Parameter	900 °C	950 °C	1000 °C	1050 °C	1100 °C
a (Å)	3.9904 (1)	3.9904 (1)	3.9894 (1)	3.9889 (1)	3.9907(1)
Volume (Å^3)	63.56 (1)	63.54 (1)	63.49 (1)	63.47	63.55(1)
1a Co/Fe occ.	0.8/0.2	0.8/0.2	0.8/0.2	0.8/0.2	0.8/0.2
1b Ba/Sr occ.	0.5/0.5	0.5/0.5	0.5/0.5	0.5/0.5	0.5/0.5
3c O occ.	1.0	1.0	1.0	1.0	1.0
1a Ba U_{iso}	0.01893 (1)	0.03687 (1)	0.01689(1)	0.00939(1)	0.01131(1)
1a Sr U_{iso}	0.02505 (1)	0.02353(1)	0.02535(1)	0.02613(1)	0.02545(1)
1b Co U_{iso}	0.03676 (1)	0.01887(1)	0.02173(1)	0.03432(1)	0.03865(1)
Ib FeU_{iso}	0.02463 (1)	0.02542(1)	0.02494(1)	0.02270(1)	0.02104(1)
3c O U_{iso}	0.06495 (1)	0.06488(1)	0.06677(1)	0.05628(1)	0.05170(1)
R_{wp}	7.51 %	7.59 %	5.60 %	12.77 %	9.92 %
R_p	5.01 %	4.99 %	4.52 %	8.68 %	7.92 %
χ^2	1.247	1.225	0.920	1.970	1.203
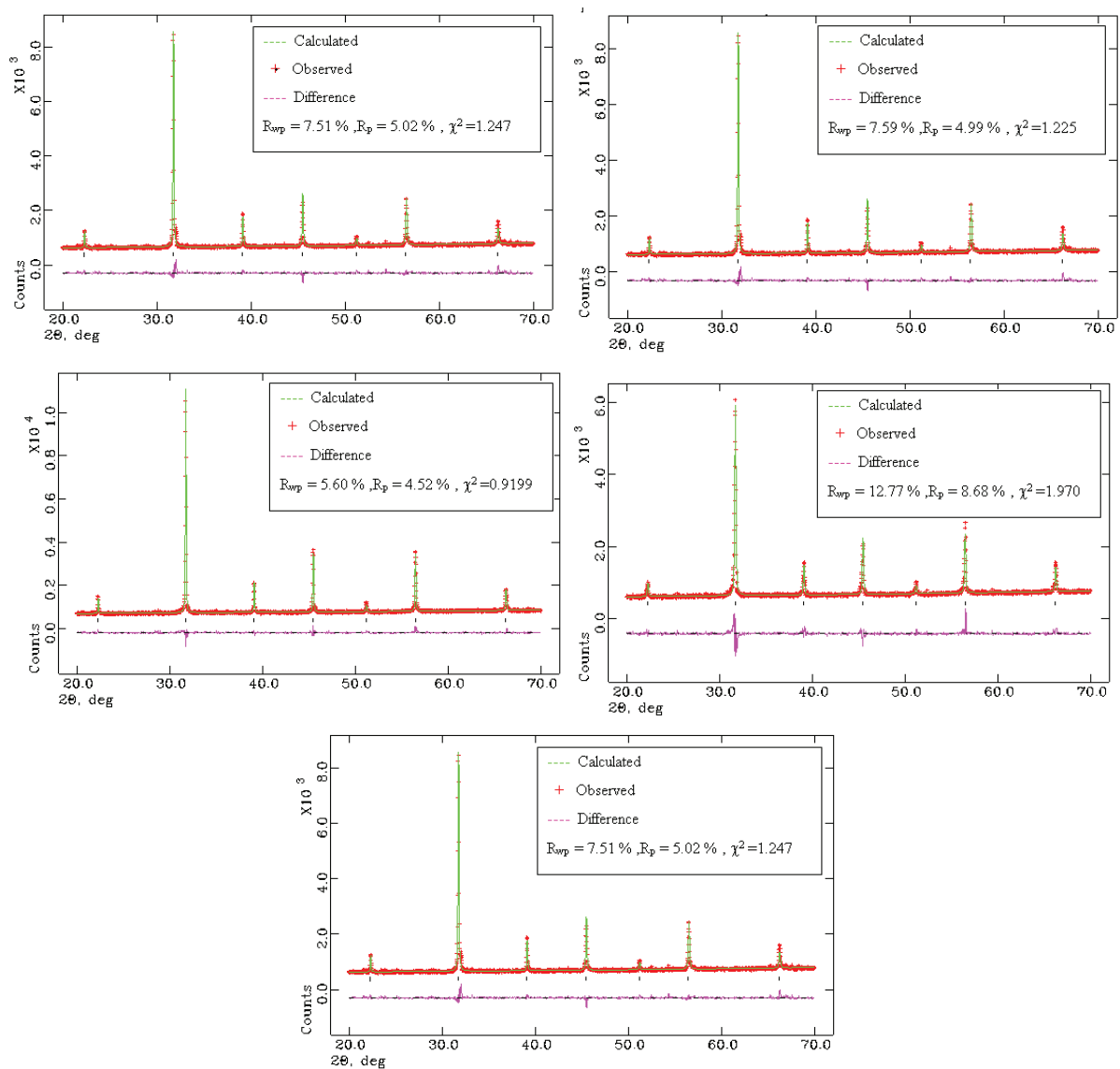
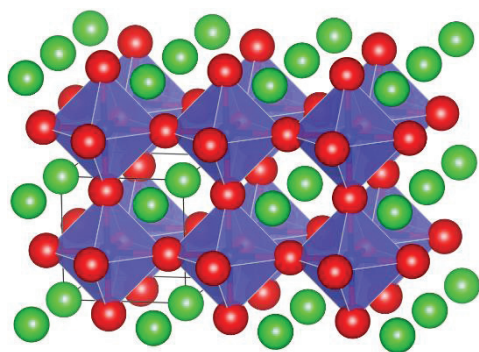**FIGURE 4.** The Rietveld plot of the $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ heated between 900 and 1100 ˚C.

FIGURE 5. The atomistic modelling of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$.

CONCLUSION

The optimum temperature for preparing $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ is 950ºC. Below than that, the reaction could be obtained but require longer period of time to complete the reaction (more than 15 hours at 900ºC). Crystal structure of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was obtained through Rietveld refinement of XRD data. The final refined structural model shows very small disagreement (χ^2 are about 1.2 except for 1050ºC) between calculated and observed patterns as illustrated in Figure 4.

ACKNOWLEDGMENTS

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