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SYNTHESIS AND CHARACTERISATION OF $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ AS CATHODE MATERIALS FOR SOLID OXIDE FUEL CELLS APPLICATION

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ABSTRACT

$Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ was successfully synthesized using modified solid-state synthesis method. Pure phase $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ could be obtained after heated at 900 °C for 15 hours and their structure remains stable up to 1050 °C in air. The lattice parameters and unit cell volume slightly expanded at 1000 °C and above. The crystallite size was significantly increased as temperature increased.

Keywords: Solid oxide fuel cells, cathode materials, $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$

INTRODUCTION

Solid oxide fuel cells (SOFCs) are potential clean energy resources for the green and sustainable technology development, particularly for transportation sectors. SOFCs convert chemical energy to electrical energy without producing any harmful by-products. Conventional SOFCs commonly operated between 800° and 1000 °C. However, the current technology enabled SOFCs operate at relatively lower temperature ranges between 500° and 800 °C, known as Intermediate Temperature SOFCs (IT-SOFCs). The IT-SOFCs offer huge advantages by reducing operational cost and expand the limit for materials' selection [1,2]. But, the catalytic activities of the existing cathodes and electrolytes slightly reduced. Thus, intensive researches are carried out to obtain the best possible cathodes and electrolytes for IT-SOFCs.

$Ba_{1/2}Sr_{1/2}Co_{0.8}Fe_{0.2}O_{3-\delta}$ has attracted great attentions as a potential cathode material for IT-SOFCs [3]. It is perovskite-type cathode materials with the space group of Pm3m. It exhibits high ionic conductivity and large oxygen diffusion rate at temperature between 500° and 800 °C [4]. The existing of oxygen non-stoichiometry in the crystal lattices contributes to the large oxygen diffusion rate. Therefore, the transition metal elements in the compound oxidized of to remain their electroneutrality and resulting mixed ionic and electronic conductivities occurred at high temperatures. This paper presents the structure and crystallographic properties of $Ba_{1/2}Sr_{1/2}Co_{0.6}Fe_{0.4}O_{3-\delta}$ as a cathode material for IT-SOFCs. It is analogous for the $Ba_{1/2}Sr_{1/2}Co_{0.8}Fe_{0.2}O_{3-\delta}$ with reducing Co contents. The different Co:Fe ratio's may affect their properties as a function of temperature.

EXPERIMENTAL

$Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ powders were prepared using combined EDTA-citrate complexing sol-gel and followed by solid-state synthesis method. Metal nitrates $Ba(NO_3)_2$ (Qrec, 98%), $Sr(NO_3)_2$ (HmBG, 98%), $Co(NO_3)_2.6H_2O$ (HmBG, 98%), and $Fe(NO_3)_3.9H_2O$ (HmBG, 98%) were used as starting reagents. Initially, EDTA was dissolved in ammonia solution to form EDTA-NH_3OH solution. A stoichiometric amount of metals nitrates were dissolved in de-ionized water in a beaker. The EDTA and citric acid as complexing agents were added. The molar ratio the amount of metal nitrate: EDTA: citric acid was fixed as 1:1:1.5. Then, ammonia solution was added into the solution to control pH to ~6. After that, the beaker was placed on a hotplate with magnetic stirrer. The solution was stirred and heated up to 95 °C until it became a viscous dark-red gel. The gel was dried in oven at 180°C for 12 hours, followed by firing up to 260 °C for 5 hours to remove all inorganic contents. The fired product in the beaker was removed and ground using pestle and mortar. The obtained powder was heated for between 900 and 1050 °C with intermittence grinding.

The purity of products were 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 $2\theta = 20^{o}$ and 70^{o} 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 prepared samples [6].

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for the samples that were heated between 900° and 1050 °C. The diffraction patterns are similar as reported in literatures and were matched with the ICDD database (No.: 00-055-0563). All reflections are sharp and well defined signify high crystalline powder samples. The reflections remain stables as a function of temperature. All the XRD data were indexed using least-square refinement with the space group of Pm-3m. Results show that the powder possesses cubic perovskite symmetry with primitive crystal lattice.

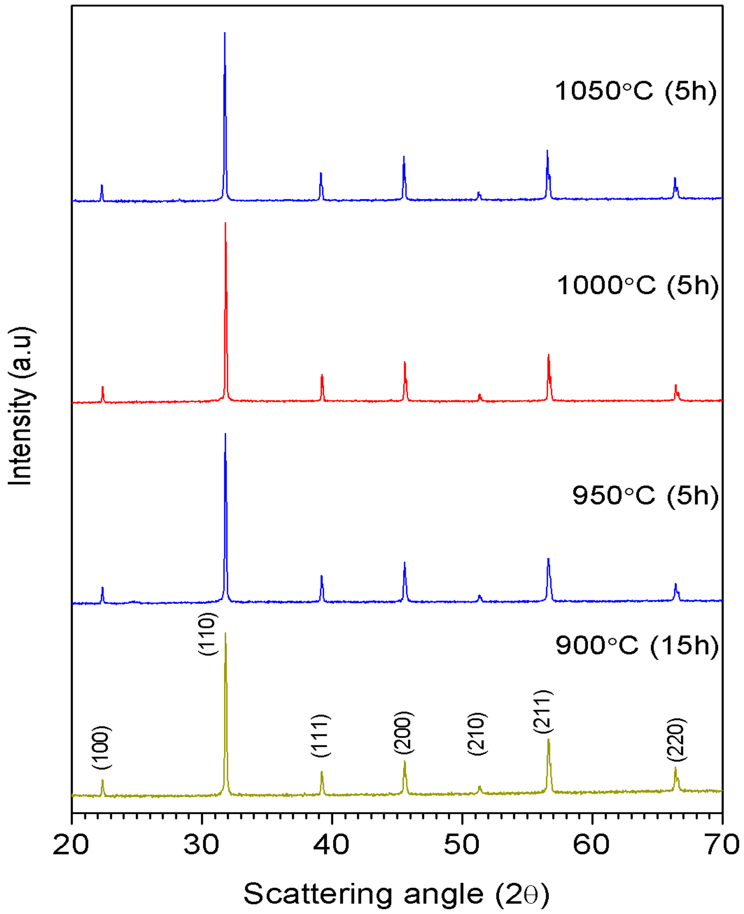


Figure 1: XRD pattern of $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ heated between 900 and 1050 °C in air.

Figure 2 shows the lattice parameters of the indexed XRD patterns as a function of temperature. The result shows that lattice parameters for sample that heated at 900° and 950 °C are similar within errors. At 1000 °C, the lattice parameters slightly increased and then remain similar within errors at 1050 °C. The changes in lattice parameter and unit cell volume may contributed by changing of δ in the $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$

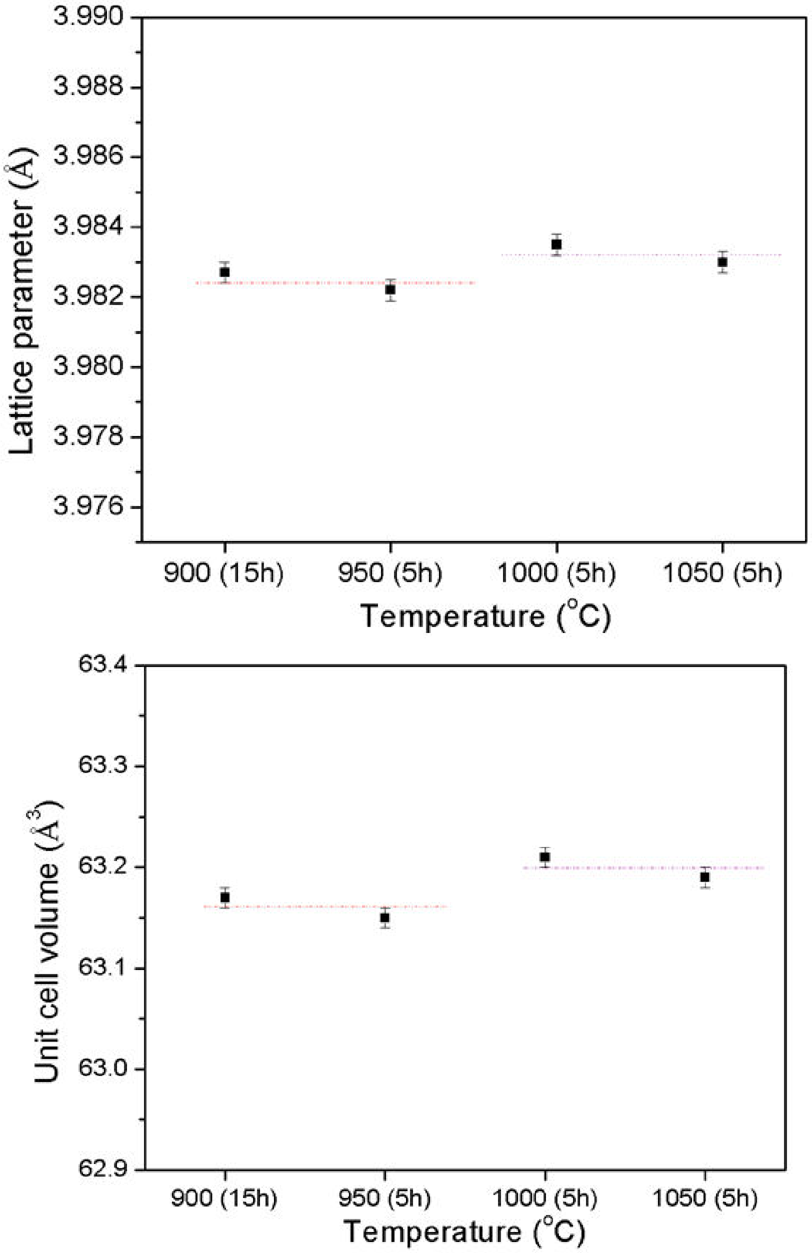


Figure 2: The lattice parameter and unit cell volume of $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ heated between 900° and 1000 °C in air

Table 1 shows the crystallite size of the powder samples that were calculated by using Scherer equation for FWHM (full width half maximum) and integral breadth of reflection (110). The Scherer equation used as below:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

The results show that the crystallite size was increased significantly as firing temperature increased.

Table 1: Crystallite size for $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ heated between 900° and 1050 °C in air.

Temperature (°C)	900 (15 h)	950 (5 h)	1000 (5 h)	1050 (5h)
Crystallite size (FWHM)	597.8 (0.154)	611.3 (0.150)	653.0 (0.133)	690.9 (0.141)
Crystallite size (Integral Breadth)	513.3 (0.100)	540.3 (0.170)	594.6 (0.142)	646.6 (0.142)

Rietveld refinement of $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ were performed to identify any changes in crystallographic properties. Table 2 shows the initial structure model with the space group of Pm3m that obtained from ICSD database (ICSD No.: 109462) was used as in all subsequent refinements. Generally, Ba and Sr are shared at the same position (0,0,0), which is considered as A-site, located at the edge of unit cell. While, Co and and Fe also shared at the same position (½, ½, ½), which is considered as B-site, located at the centre of unit cell. While, O located at the position (½, ½, 0). An isotropic displacement parameter (U_{iso}) for all atoms is fixed as 0.01 as our XRD is not sensitive to determine the U_{iso}.

Table 2: The initial model of Structure Refinement of $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$

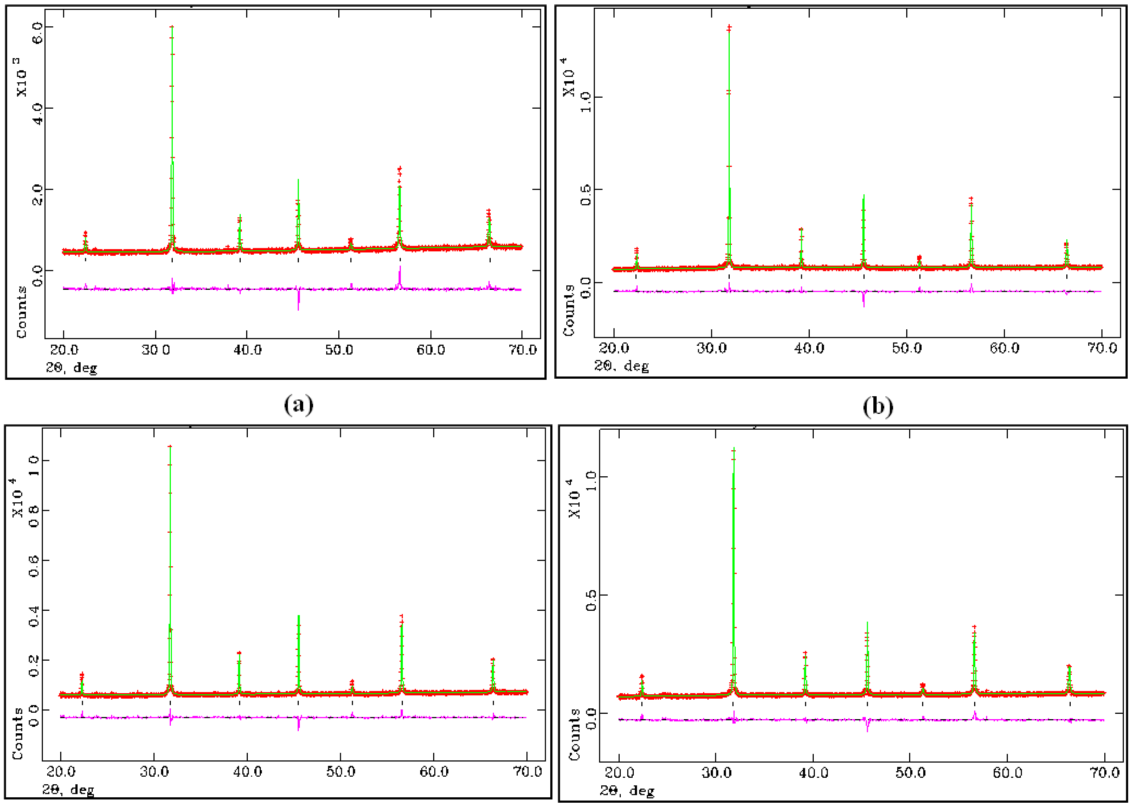
Atom	Wyckoff Position	Atomic position (x,y,z)	Occupancy	Isotropic displacement parameter (U_{iso} x 100) (Å^2)
Ba	1b	0,0,0	0.500	0.01
Sr	1b	0,0,0	0.500	0.01
Co	1a	½,½,½	0.60	0.01
Fe	1a	½,½,½	0.40	0.01
O	3d	½,½,0	1.00	0.01

Table 3: Structural refinement data for $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ as a function of temperature

Temperature (°C)	900°C (15 hours)	950°C (5 hours)	1000°C (5 hours)	1050°C (5 hours)
Lattice parameter (Å)	3.9820 (1)	3.9810 (1)	3.9815 (1)	3.9823 (1)
Unit cell volume (Å^3)	63.14 (1)	63.09 (1)	63.12 (1)	63.15 (1)
R_p	7.38 %	4.76 %	5.63 %	5.35 %
R_{wp}	5.04 %	3.63 %	3.94 %	3.81 %
χ^2	1.388	1.002	1.317	1.033

Figure 4 shows the pattern fit of refined structure model obtained from Rietveld refinements. The pattern fit was plotted as observed (red), calculated (green) and differences plot (purple). The result denoted that the intensity mismatch for the sample that prepared at 900 °C is quite obvious at 2θ = 45.56 and 56.64°, respectively. However, the disagreement between calculated and observed patterns is getting smaller for samples that heated between 950° and 1050 °C.

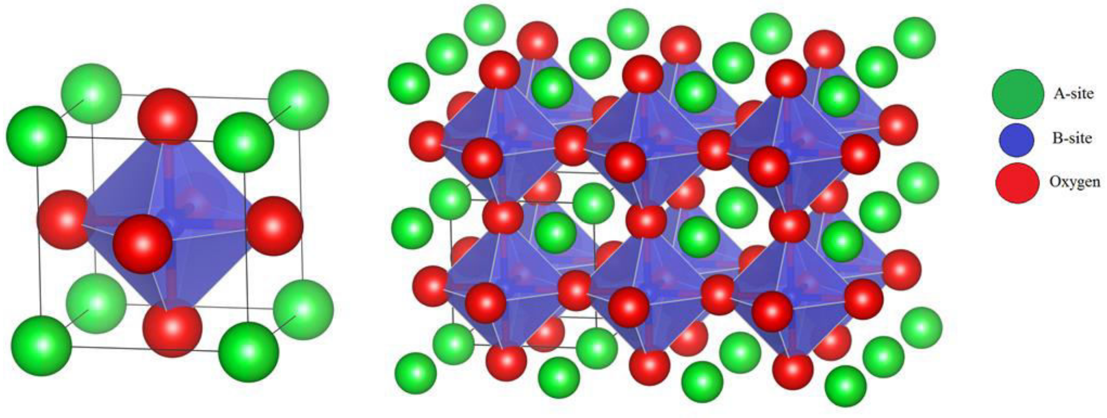
Figure 5 shows the atomic simulation of the refined structural model of $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$. The green balls represent Ba and Sr atoms that are located at the edge of unit cell. While, the red balls that placed on each face of unit cell represent O atoms. Furthermore, the blue 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.



(a) **(b)**

(c) **(d)**

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 1000 °C



(a) (b)

Figure 5: The atomistic modelling of $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$

CONCLUSION

The optimum synthesis temperature to obtain phase pure $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ prepared using modified sol-gel method and followed by solid-state synthesis is at 900 ^{o}C and above. Lattice parameter and unit cell volume slightly increased but the crystallite size increased significantly as a function of temperature. The atomistic model that illustrated from the refined structure model clearly showed that $Ba_{0.5}Sr_{0.5}Co_{0.6}Fe_{0.4}O_{3-\delta}$ has a stable cubic crystal with the primitive-type lattice.

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