COMPARISON OF La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ PEROVSKITE SYNTHESIS METHODS AND THEIR EFFECT ON THE PARTICLE SIZE

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ABSTRACT

The dense structure required by mixed-ionic and electronic conducting (MIEC) membrane based on La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF) material could be influenced by the particle size of the LSCF, as this densification involves sintering of the particles. The particle size could be determined by using an appropriate synthesis method. The aim of this work is to investigate the effect of synthesis method to the particle size of the resulted powders. In this work, LSCF was successfully synthesized by sol-gel, co-precipitation, and solid-state methods. The co-precipitation is carried out with and without aging treatment after addition of precipitating agent. All LSCFs have a structure similar to the LaCoO$_3$ structure as mother compound. Solid-state and co-precipitation with aging treatment can produce LSCF with high purity. Meanwhile, there were still other phases in LSCFs which were synthesized by sol-gel and co-precipitation methods without aging treatment. Other phases that appear are estimated from the Co$_3$O$_4$ for co-precipitation method without aging treatment and Co$_3$O$_4$ and Fe$_2$O$_3$ for sol-gel method. The solid-state method is capable of producing particles with the highest crystallinity compared to other methods. The TGA results from LSCF with the sol-gel method and co-precipitation (without and with aging time) showed that the perovskite could be formed at temperature 650 °C. Characterization of LSCF particles with Scanning Electron Microscope (SEM) showed that all samples had irregular particle shapes, with uniformly small particle for sol-gel method, and the possibility of formation of large particle for co-precipitation method. However, Particle Size Analysis (PSA) analysis shows that in general, the co-precipitation method could produce smaller particle (particle size 1904.1 nm) than the solid-state method (particle size 2812.4 nm).

Keywords: Synthesis, La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$, Co-precipitation, Solid-State, Sol-gel

INTRODUCTION

Mixed Ionic and Electronic Conducting (MIEC) membrane is a promising membrane technology that can be used for several applications, such as the production of pure oxygen from air and conversion of methane to be syngas or methanol[1,2]. One of the most promising membrane material is perovskite oxide[3–5]. This material has the general formula of ABO$_3$, where A-site comes from alkaline, earth alkaline, rare earth ion or its combination and B-site comes from transition metal ions. This perovskite membrane has good mechanical stability, excellent stability at high temperature and high oxygen permeability[1,6–8]. Among perovskite family, lanthanum-based membrane material, or well known as La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF), also exhibits high stability toward reducing atmosphere[9,10].

The MIEC membrane should be prepared in the form of a dense membrane to make sure that oxygen could pass the membrane in the ionic form (O^{2-}). Several methods have been developed for preparing dense LSCF membrane, for example, dry pressing method and phase inversion method. Despite the different procedure and concept, both methods require a sintering process at high temperature for densification process[6]. The densification process is influenced by several factors, for example, the given pressure (for dry pressing method), sintering temperature and particle size of the membranes. Among

these factors, the particle size of the membrane is considered as crucial points because the densification of the membrane during sintering occurs on each LSCF particle. This particle size of perovskite material could be influenced by the synthesis method of the LSCF because each synthesis method could produce LSCF with different particle size[2,11].

In LSCF synthesis, the inappropriate cation amount results in the formation of undesirable phases other than perovskite structure. Under the same operating conditions, the use of different synthesis methods may cause different oxygen permeation flux values. Obviously, the unique microstructure produced by each method has an effect on ionic and electronic conductivity of materials[2]. Each synthesis method will produce different particle sizes and shapes. The difference in the shape and size of the particles will affect the morphology and mechanical strength of the produced membrane[12]. Particle size that is too large will cause interaction and compaction during sintering process not to occur optimally so that it still produces pores. In addition, particle size will also affect the size of the grain boundary on the membrane thus affecting the oxygen permeability. Yao *et al.* previously report, in spite of densification issue, the large particle size increases the oxygen permeability when the diffusion of oxygen ion is faster in the bulk particle rather than in the grain boundary[13]. However, the membrane should be convinced dense first.

Up to now, many methods can be used to synthesize perovskite oxides for example solid-state, precipitation, co-precipitation, hydrothermal, combustion route and sol-gel processes[2,12,14,15]. Solid-state, sol-gel, and co-precipitation methods are relatively easy methods with high purity product compare to the other methods. The advantage of using solid-state method is the ability to produce products with large yield and high crystallinity[16]. However, this method requires high temperatures and produces large particle size. Sol-gel and co-precipitation method could also produce high purity perovskite. But in both methods, it requires some controls over certain parameters and is relatively more complex than solid-state method[12]. The imperfect reaction during the synthesis using sol-gel and co-precipitation method, as well as the inappropriate step could result in the formation of other phase rather than LSCF, or sometimes, the formation of oxide compound form of its constituent cations. The advantage of these two methods is that they can produce small and uniform powder particles[4,10].

The synthesis of perovskite with various methods has been reported by many researchers. However, these reports mainly use the synthesis method as a supplementary step for their works in preparing the MIEC membrane. The synthesis method itself, the detail steps along with the accompanying phenomenon and the effect on the yielded product are rarely discussed. In this work, we focus on the comparison of LSCF synthesis methods in relation to the yielded particle properties. This is important because different synthesis method could produce the different character of the LSCF particles, such as structural phases, crystallinity, shape, and size of the particles. In this works, the LSCF oxide was synthesized using three different methods, i.e., sol-gel, co-precipitation and solid-state method. The synthesis process and the phenomena that occurred during synthesis that is predicted to influence the formation of the desired product are discussed. The yielded LSCF particles especially in the term of structural phases, crystallinity, shape, and size of the particles are also discussed. This report is expected to give guidance in the election of the appropriate method in preparing LSCF powders for certain application.

EXPERIMENTAL

Material
The materials used for solid-state method were lanthanum oxide (La_2O_3) (Merck) p.a. 99.9%, cobalt oxide (Co_3O_4) p.a. 99.5% (Aldrich), strontium carbonate ($SrCO_3$) p.a. 99.9% (Aldrich), and iron oxide (Fe_2O_3) p.a. 97% (SAP Chemicals). Meanwhile, the synthesis with the sol-gel and co-precipitation method was carried out with reactants such as lanthanum oxide (La_2O_3) (Merck) p.a. 99.9%, strontium nitrate ($Sr(NO_3)_2$) p.a. 99.0% (Merck), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) p.a. 99.5% (Aldrich), iron nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) p.a. 97% (Aldrich), HNO_3 p.a. 65% (Mallinckrodt chemical), methanol (SIP Chemical) and aqua demineralized (Aqua DM). Citric acid $H_3C_6H_5O_7 \cdot H_2O$ 100% (Mallinckrodt) used for the sol-gel method, and NaOH (Aldrich) for co-precipitation method.

Synthesis of LSCF by Sol-gel method
The LSCF perovskite oxide was synthesized by sol-gel method as reported by Ningrum and Fansuri (2010)[17]. The synthesis process was begun by dissolving the stoichiometric amount of reactants such us

La$_2$O$_3$ into 10 mL HNO$_3$ 1.0 M, Sr(NO$_3$)$_2$ into 8 mL aqua DM, Co(NO$_3$)$_2$·6H$_2$O into 5 mL aqua DM and Fe(NO$_3$)$_3$·9H$_2$O into 12 mL aqua DM. Each reactant solution is then mixed consecutively and then stirred. After completely mixed, 2 mL citric acid was added drop by drop the mixture under stirring. The resulted mixture is then stirred with a magnetic stirrer for an hour and evaporated over the hotplate at a temperature of 85 °C until the solution becomes homogeneous and brown gel (xerogel) is formed. Next, xerogel is dried in an oven for ± 24 hours at 105 °C. The obtained powders were ground and calcined at a temperature of 750 °C for 5 hours. The calcined powder is then characterized using X-ray Diffractometer (XRD). The shape and morphology of the particle are examined using SEM. In addition, the calcination temperature was determined from the Thermogravimetric (TG) analysis of the precursor (xerogel).

Synthesis of LSCF by Co-precipitation Method
The LSCF perovskite oxide was synthesized by co-precipitation method as reported by Thoriyah and Fansuri (2010)[18]. Two synthesis procedures were performed in this method, *i.e.* with and without aging treatment after addition of precipitating agent (NaOH). For co-precipitation method without aging treatment, the synthesis process was started by dissolving the stoichiometric amount of La$_2$O$_3$ into 5 mL HNO$_3$ 1.0 M, Sr(NO$_3$)$_2$ into 5 mL aqua DM, Co(NO$_3$)$_2$·6H$_2$O into 5 mL aqua DM and Fe(NO$_3$)$_3$·9H$_2$O into 10 mL aqua DM. Each reactant was then mixed consecutively and stirred for 30 minutes. After 30 minutes of stirring, the NaOH 2 M was added drop by drop excessively until the pH reached 6-7 under stirring. The stirring was continued for 1 hour. The resulted precipitate (precursor) was filtered and washed using methanol. The obtained precursor was then heated at 105 °C for 24 hours. The dried precursor was then calcined at 750 °C for 5 hours. The resulted precursor from this method was analyzed using XRD and SEM. Calcination temperature was determined from the Thermogravimetric (TG) analysis of the precursor.
The synthesis of LSCF by co-precipitation method with aging treatment is performed with similar reactants, amount of reactants and steps just like in co-precipitation method without aging treatment. However, in this method, the mixture of the reactant was aged for 35 hours after the addition of NaOH solution. The resulted precursor from this method was analyzed using XRD, SEM and Particle Size Analyzer (PSA).

Synthesis of LSCF by Solid-State Method
The LSCF perovskite oxide was synthesized by a solid-state method as reported by Aliyatulmuna *et al.*, 2017[9]. All reactants were firstly heated in the oven at 105 °C for 1 hour to remove the adsorbed water in reactant powder. After heating, the reactants were then cooled in the desiccator. The synthesis process was begun by weighing and mixing the stoichiometric amount of La$_2$O$_3$, SrCO$_3$, Co$_3$O$_4$, and Fe$_2$O$_3$. The reactants were then ground together for 2 hours to form a homogeneous mixture. The homogeneous mixture was then calcined at 900 °C for 2 hours. During this calcination process, the heating was held for 1 hour at 400 °C before continuing it to 900 °C. This first calcination process was performed twice. The calcined powders obtained from the first calcination process was then ground again and further calcined at 1000 °C for 2 hours. This second calcination process is carried out twice also. Thus, a total of calcination process was 4 hours for each first (900 °C) and second (1000 °C) calcinations, respectively. The intermediate grinding was applied between each calcination process. The heating rate for this calcination is 3 °C/minute. The resulted powders were characterized using XRD, SEM dan PSA.

Characterization
The crystal structure of all resulted LSCF was characterized by X-ray diffraction (XRD JEOL JDX-3530). The sample is placed in a sample holder and then is irradiated with CuKα (λ=1.54056 Å). Diffraction data are taken in the range 2θ of 20 to 100° with a step size 0.02 °/second. The obtained XRD pattern is then matched with the standard data from the PDF (Powder Diffraction File) card issued by JCPDS (Joint Committee on Powder Diffraction Standard).
The crystallinity of the samples was determined based on the relative intensity [19]. The relative intensity of the samples was calculated based on the highest peak of perovskite at 2θ around 32° and used XRD

pattern obtained from a solid-state reaction. The relative intensity was calculated using Equ.-1, where I_{sample} was the intensity of the calculated sample, and $I_{Reference}$ is the intensity of the solid-state.

$$Relative\ intensity = \frac{I_{sample}}{I_{reference}} \times 100\%$$

(1)

The crystallite size (D) of the sample was calculated using the Scherrer formula as shown in Equ.-2[20]. The $k = 0.9$ refers to a shape factor, λ is wavelength of the X-ray irradiation (1.54056 Å), B is Full Width at Half Maximum (FWHM) in radians and θ is Bragg angle.

(2)

$$D = \frac{k\,\lambda}{\beta\,cos\theta}$$

The particle size of perovskite powders was characterized using Particle Size Analyzer (PSA Horriba Scientific SZ-100). A certain amount of LSCF was dispersed in methanol solution to form a stable suspension. The suspension was then placed to the sample holder and was analyzed.

The particle shape and morphology of the obtained LSCF powders were observed using Scanning Electron Microscope (SEM Zeiss EVO MA-10). Samples powders were placed on the sample pins, then the pins are placed in the SEM sample chamber for the scanning process. The scanning process is carried out with an accelerating voltage of 15-20 kEV with a SE1 detector.

RESULTS AND DISCUSSION

Synthesis of LSCF

LSCF perovskite oxide was synthesized by the sol-gel method using La_2O_3, $Sr(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ as reactants. Lanthanum nitrate solution was made by dissolving lanthanum oxide powder in HNO_3 1 M. HNO_3 was chosen as a solvent because La_2O_3 could optimally dissolve in HNO_3. The process of La_2O_3 dissolution was carried out by constant stirring using a magnetic stirrer at a temperature of 60 °C with speed of 400 rpm until all La_2O_3 powders dissolved and form clear $La(NO_3)_3$ solution. The other three reactants, namely $Sr(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, are the source of Sr^{2+}, Co^{3+}, Fe^{3+} ions, respectively. They were dissolved in aqua DM. The reaction process was started by mixing all reactant solutions into a glass beaker under stirring. This process produces a solution (sol). The stirring process was continued for 30 minutes. The citric acid solution was then added with the ratio between all total metal ions and citric acid was 1:1[21]. The solution was then stirred continuously on the hotplate at 85 °C to form xerogel. The resulting xerogel was dried for 24 hours at 105 °C. This process produced a reddish-brown powder. The resulting powder was then calcined at a temperature of 750 °C for 5 hours. The yielded product from each step of this sol-gel is shown in Fig.-1.
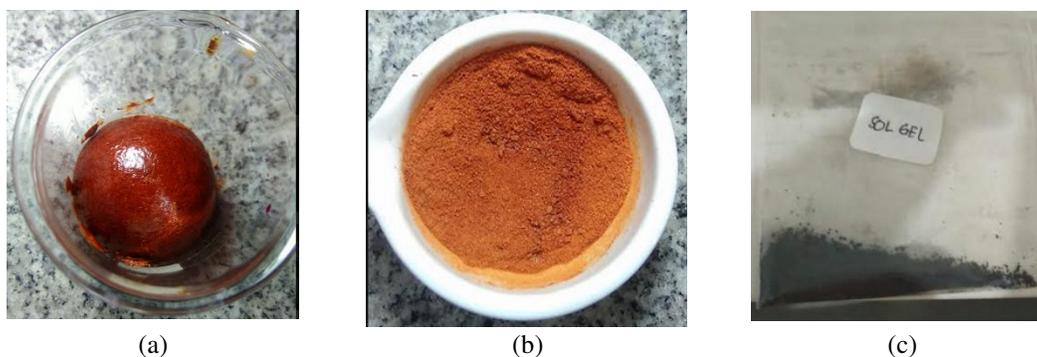

Fig.-1: (a) Xerogel, (b) Precursor Powders after Heating and (c) LSCF after Calcination

The synthesis of LSCF by co-precipitation method used similar reactants just like in the sol-gel method. However, the clear difference is in the usage of NaOH as a precipitating agent. After the addition of the NaOH solution, the red-brown precipitate was formed. This precipitate was directly filtered and was

heated until dried powder (precursor) was formed. The precursor was then calcined at 750 °C for 5 hours similar to the sol-gel method.

In earlier co-precipitation method, filtrate color is still brownish which indicates that there is still possibly ions component in the filtrate. This is feared to affect the composition of the LSCF resulting in the formation of other phase or impurity. Therefore, the synthesis of LSCF was also carried out by applying aging treatment after the addition of NaOH solution to the reactants mixture. This treatment is done to optimize the precipitation reaction thus the total amount of reacted cations are in good accordance with the stoichiometric ions. This aging treatment was successfully made the filtrate to be colorless and clear indicating that the ions are completely reacted or precipitated. The resulted precursor from this process was then calcined at 750 °C for 5 hours. It was expected that no metal ions remain in the filtrate so that it can form LSCF with the right composition and structure. LSCF powder before and after calcination is shown in Fig.-2.

(a)   (b)
Fig.-2: (a) LSCF Precursor before and (b) after Calcination

In the sol-gel and co-precipitation method (both with and without aging treatment), the calcination temperature was determined using TGA. The calcination is performed after the completion of the decomposition process on LSCF precursors after heating in elevated temperature up to 1000 °C. The TGA curve of the three samples was shown in Fig.-3. Based on Fig.-3, the characteristic of the TGA curve for the three samples was quite similar. It appears that there are three weight losses during analysis. The first weight loss, that occurs at the temperature of 80-120 °C and presented as the area I, is predicted as desorption of physically adsorbed water in the precursor particles. The second weight loss around 180 – 280 °C (area II) is predicted as the releasing of crystal water that exists in the precursor. Based on this phenomenon, it is predicted that in precursor contains hydrated species (compounds) that would be the LSCF after reaching the correct temperature. The third weight loss (area III) that begins at 300-620 °C is the decomposition of citric acid that still exists in the precursor synthesized by sol-gel method, as well as the decomposition of nitrate in the precursor. The sample weight is steady after 650 °C indicating that there is no further decomposition and the reaction of perovskite formation could be started[17,18]. Based on this TGA curve, the calcination of LSCF made by sol-gel, co-precipitation with and without aging treatment was determined at 750 °C to ensure the reaction process.

The synthesis of LSCF by solid-state method was carried out using La_2O_3, $SrCO_3$, Co_3O_4, and Fe_2O_3. Before being used for synthesis, all reactants were dried in an oven at 105 °C for 1 hour to remove water that possibly adsorbed in the surface of the particles. The presence of adsorbed water could affect the true amount of the reactant, resulting in the formation of other phases or excess in other reactants[16]. After drying, the reactants were weighed according to the stoichiometric amount. The reactants were then put into the agate mortar for grinding for two hours to form homogeneous reactants mixture. The calcination process was carried out at 900 °C and further calcination at 1000 °C. The intermediate grinding was applied between each calcination process. This intermediate grinding was supposed to form a new contact area between particles thus the ionic diffusion during solid-state reaction could occur optimally[22]. In this calcination process, the process was held at 400 °C for 1 hour in the first calcination process to decompose the carbonate ions. The decomposition of carbonate ions could release carbon dioxide that

could initiate the bumping. The homogeneous reactant mixtures before and after calcination are shown in Fig.-4.
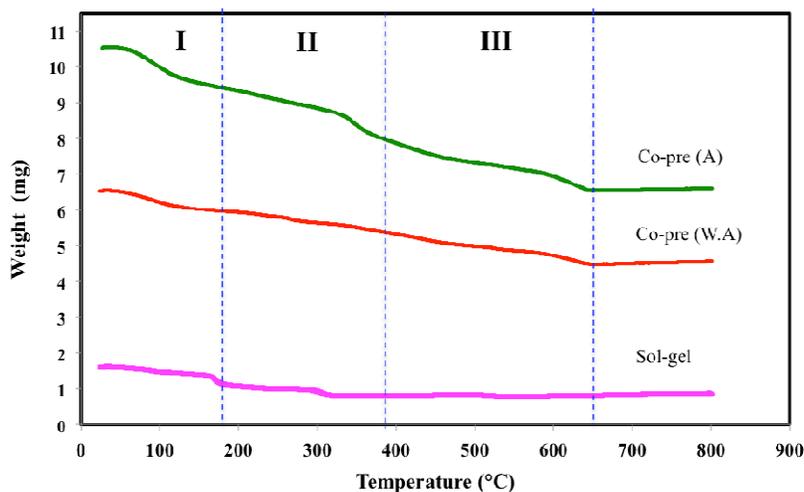

Fig.-3: TGA Curve of LSCF Precursor (Co-pre (W.A) is Co-precipitation without Aging Treatment, Co-pre (A) with Aging Treatment)
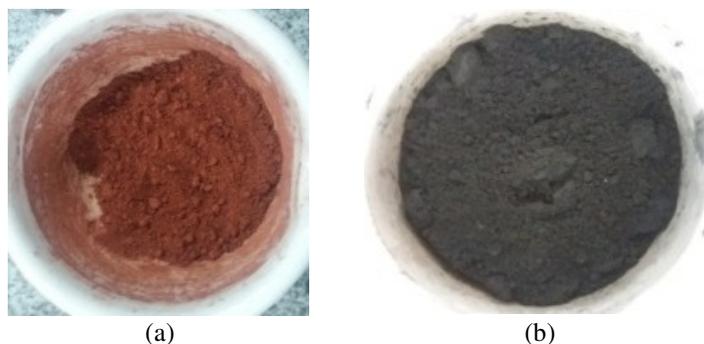

(a)   (b)

Fig.-4: (a) Homogeneous Reactants Mixture before Calcination and (b) LSCF Powders

XRD Analysis
LSCF perovskite oxides synthesized by sol-gel, co-precipitation without and with aging treatment and solid-state method were analyzed using X-ray diffraction to determine the phase formed in perovskite oxide and its crystallinity. Fig.-5 shows XRD patterns from samples synthesized by the four methods. The comparison of these XRD patterns with the reference pattern from $LaCoO_3$ as obtained from PDF Card No. 01-84-0848 shows that the four samples exhibit similar patterns with the reference pattern. The similarity as shown Fig.-5 shows that the sample has a similar structure as $LaCoO_3$ as mother compound of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF). This similarity is indicated by the sharp peaks at $2\theta = 33.05°$, $40.72°$, $47.00°$, $58.48°$, $68.61°$, and $78.04°$. Those peaks are the characteristic peaks of the $LaCoO_3$. This result shows that the perovskite structure has been formed in all samples[9,23]. The shifting of 2θ of the samples compared to the reference is caused by the substitution Sr^{2+} and Fe^{3+} in the LSCF which have different ionic radii[24].

Fig.-5 shows that XRD patterns from LSCF synthesized by solid-state method and co-precipitation with aging treatment have peaks in good agreement with the reference without any other peaks appearing. This shows that the produced LSCF has high purity without the presence of other phases. This is quite different with LSCF which are synthesized by the co-precipitation method without aging treatment and sol-gel method. There are additional peaks come from other than perovskite characteristic peaks. These peaks are predicted as peaks from Co_3O_4 as indicated by the presence of peaks at 2θ of $31.0°$, $36.6°$ and

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64.8° based on PDF card No. 01-080-1535 on the sample synthesized by co-precipitation method without aging treatment. The sample synthesized by sol-gel method exhibits Fe_2O_3 beside Co_3O_4 as indicated by the peaks at 2θ of 33.1°, 35.5° and 54.0° based on PDF card No. 00-024-0072. There are also several unidentified peaks in this sample. The presence of these phases could be caused by the cation of reactants that are not perfectly reacted[9,17]. These additional phases could be formed due to the imperfect reaction of those cations during synthesis. As seen in the synthesis process by co-precipitation method without aging treatment, the filtrate of the solution showed brownish color indicating the presence of ion in that filtrate. This caused the mismatch on the stoichiometric amount of the ions in the precipitate resulting in other phases other than the LSCF phase. Based on this result, it appears that the solid-state method is a relatively easy method to produce LSCF with high yield and purity because the procedure is simpler and the number of reactants is more stable. Meanwhile, co-precipitation and sol-gel method is the relatively complex method where the inappropriate step, procedure and amount of reactant could lead to the imperfect reaction or formation of phases other than the desired product[12].
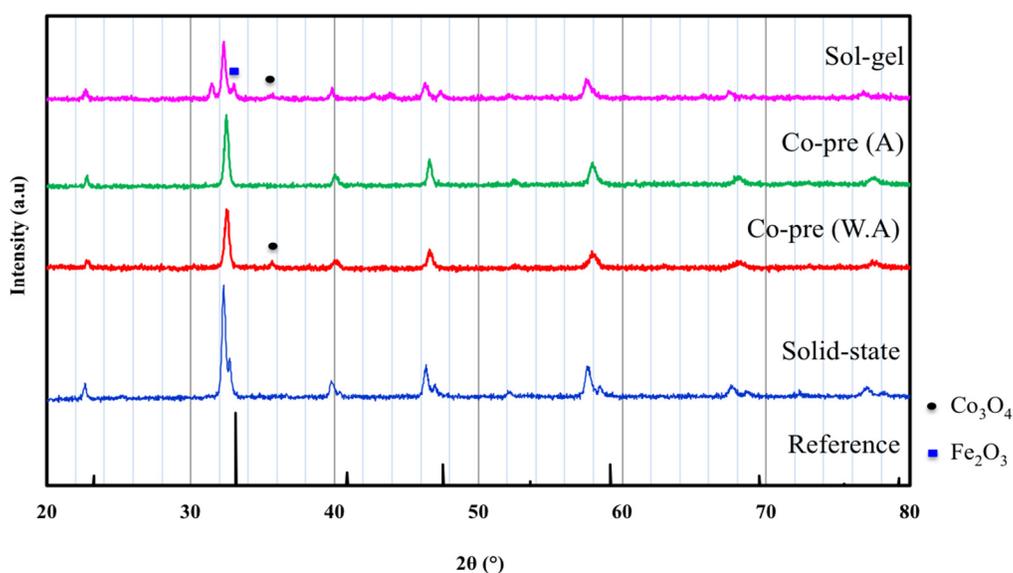

Fig.-5: XRD Patterns of the Resulted LSCF Perovskite (Co-pre (W.A) is Co-precipitation without Aging Treatment, Co-pre (A) with Aging Treatment)

The synthesis method greatly influences the crystallinity of the particles formed. The crystallinity indicates the crystal size in the particles[19]. The crystallinity of LSCF calculated based on Equ.-1 is shown in Table-1. The data in Table-1 shows that the highest crystallinity is indicated by LSCF which is synthesized by the solid-state method, with 100% relative intensity. Meanwhile, the lowest crystallinity was indicated by the sol-gel and co-precipitation method without aging treatment. The high crystallinity in the LSCF synthesized by a solid-state method is caused by the high calcination temperature. The further second calcination increases the crystallinity. While at lower calcination temperatures like the precursor route method such as sol-gel and co-precipitation, the crystal formation is not really optimal. It is predicted that to increase the crystallinity of the samples synthesized from precursor route method, the re-calcination could be done to enhance the crystal formation.

The crystallite size of the samples (*D*) was also calculated using Equ.-2. The crystallite sizes in Table-1 show that co-precipitation method using aging treatment and solid-state method have similar crystallite size, and both are the smallest among the others. It is surprising that the solid-state method has small crystallite size despite its high crystallinity. The long duration of grinding during synthesis as well as the intermediate grinding that is applied during calcination processes may reduce the crystallite size of the sample[16,22]. Furthermore, the largest crystallite size was shown by co-precipitation method without aging treatment. It seems that during the addition of precipitating agent, the precipitates are formed tremendously forming large crystallite size[18].

La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ PEROVSKITE SYNTHESIS METHODS   W. P. Utomo *et al.*

Table-1: Relative Crystallinity and Crystallite Size of the Samples

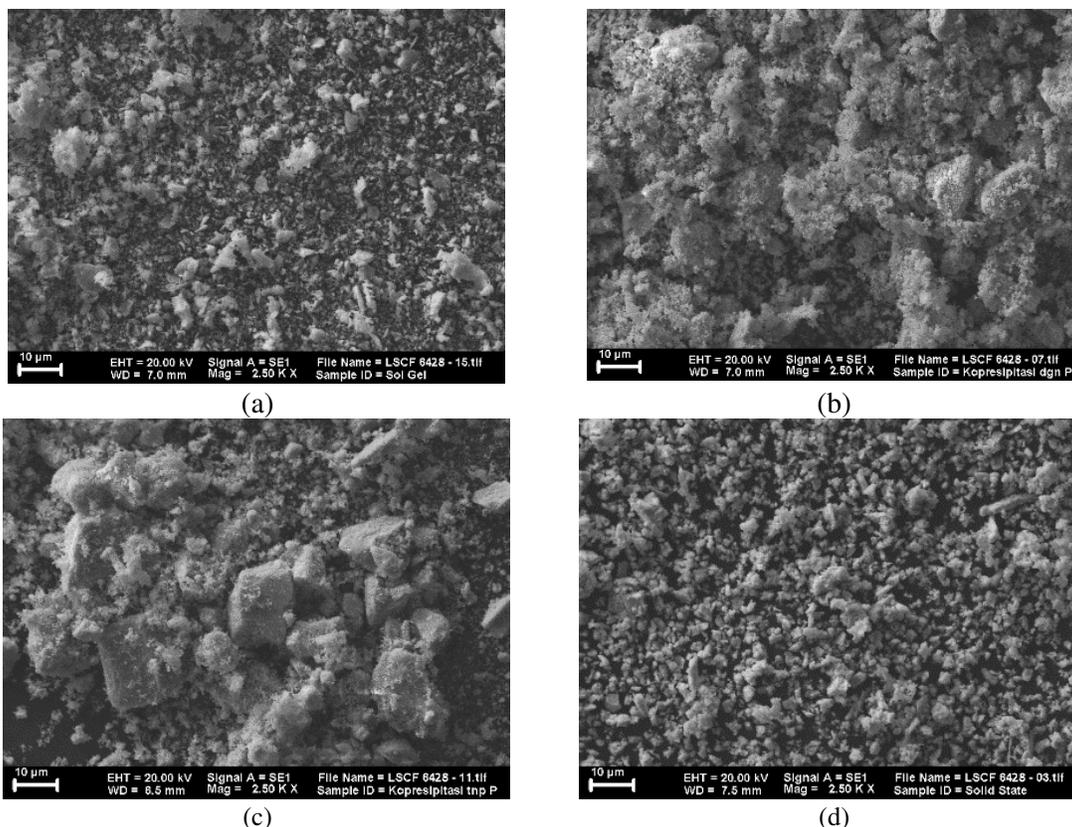| S. No.	Method	Intensity (cps)	Relative Intensity (%)	Crystallite Size (nm)
1	Sol-gel	778.89	51.40	10.36
2	Co-precipitation without aging treatment	787.08	51.94	23.59
3	Co-precipitation with aging treatment	932.46	61.54	9.58
4	Solid state	1515.23	100.00	9.58

Fig.-6: SEM images of LSCF Synthesized by (a) Sol-gel, (b) Co-precipitation without Aging Treatment, (c) Co-precipitation with Aging Treatment and (d) Solid-state Method

PSA Analysis

The analysis using Particle Size Analyzer (PSA) is aimed to know the average particle size of the synthesized LSCF. This analysis is carried to the LSCF synthesized by solid-state method and co-precipitation with aging treatment method as these sample exhibit high purity. The average particle size of LSCF synthesized by solid-state method is 2812.4 nm, so much larger than co-precipitation with aging treatment which has average particle size is 1904.1 nm. Though the samples prepared from the two methods have similar crystallite size, the particle size is different as particle size could be composed of two or more crystallite[25]. The larger particles produced by a solid-state method is quite reasonable as the solid-state method involve the utilization of reactant in the solid form that could be having large particle. The calcination process sometimes could be accompanied by the sintering of the particle resulting larger particle. This is predicted as the main cause of the large particle in spite of its small crystallite size. On the other hand, the co-precipitation method is the precursor route method, where the precursor is formed from the reaction in the form of solution. Thus, the solid particles are formed from the smallest particles. Based on this reason, co-precipitation with aging time method is suggested for the preparation of nanoparticle material.

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ PEROVSKITE SYNTHESIS METHODS   W. P. Utomo *et al.*

SEM Analysis
SEM analysis is carried out to examine the particle shape and morphology as well as to confirm the PSA result. Fig.-6 shows that in general, all samples have an irregular shape. With the similar magnification for each figure, it appears that the particle size of LSCF synthesized by co-precipitation method (for both with and without aging treatment) is larger than solid-state and sol-gel methods. It forms aggregates. This result is reasonable for comparison of co-precipitation and sol-gel. However, this result seems to be contradictive with the PSA result. The SEM image is taken from a very limited area compared to the PSA analysis. Thus, the bigger particle size as appeared in the co-precipitation method could not a representation of average size, whereas, the PSA calculate the average particle size. However, the interesting point here is that the co-precipitation method could lead to the formation of large particle than that expected. Thus, the control in aging treatment and calcination process should be highly considered in preparing smaller particles for example for preparing nanomaterial.

CONCLUSION
LSCF perovskite oxide was successfully synthesized by sol-gel, co-precipitation with and without aging treatment and solid-state methods. The co-precipitation method with aging treatment and solid-state method succeed at producing LSCF with high purity. No other phases ware found in the samples prepared by those two methods. Meanwhile, LSCF synthesized by sol-gel and co-precipitation without aging treatment has a low purity as evidenced by the presence of other phases in the samples. The solid-state method is the simplest method to produce LSCF with high purity and crystallinity, but the large size particle was formed. Precursor route method (sol-gel and co-precipitation) could produce smaller particle although this method needs extra carefully treatment during the synthesis process. The improper step or technique could lead to the imperfect reaction and forms phases other that desired product.

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