

## Synthesis of Nano-Structured $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ Perovskite by Co-Precipitation Method

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### Abstract

Nano-structured lanthanum strontium cobalt ferrite,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (LSCF), was successfully synthesized via co-precipitation method using metal nitrates as starting materials. Effects of precipitating agent and calcination temperature on the phase composition and morphology of synthesized powders were systematically studied using X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM), respectively. XRD analysis revealed that a single phase  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  perovskite was obtained in the processed sample using ammonium carbonate as precipitating agent with a  $\text{NH}_4^+/\text{NO}_3^-$  molar ratio of 2 after calcination at  $1000^\circ\text{C}$  for 1 h. The phase composition of products was also affected by changing pH values. Moreover, using sodium hydroxide as a precipitant resulted in a mixture of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  and cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) phases. Careless washing of the precursors can also led to the formation of mixed phase after calcination of final powders. Mean crystallite size of the obtained powders was not noticeably affected by varying calcination temperature from  $900$  to  $1050^\circ\text{C}$  and remained almost the same at  $10$  nm, however increasing calcination temperature to  $1100^\circ\text{C}$  resulted in sharp structural coarsening. FESEM studies demonstrate that relatively uniform particles with mean particle size of  $90$  nm were obtained in the sample processed with a  $\text{NH}_4^+/\text{NO}_3^-$  molar ratio of 2 after calcination at  $1000^\circ\text{C}$  for 1 h.

**Keywords:** *ammonium carbonate, co-precipitation,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ , nanoparticles, solid oxide fuel cell.*

### 1. Introduction

Perovskite-type complex oxides are of great interest in recent years due to their fantastic properties and various applications [1]. The ability of perovskite oxide materials to show high ionic and electric conduction as well as

appropriate catalytic activity in both oxidizing and reducing environments makes them very promising materials to be used in solid oxide fuel cells (SOFCs) as the main materials for anode, cathode or electrolyte components.

Fuel cells with the ability of directly converting chemical energy into electricity offer a clean and renewable route with high efficiencies for future power generation systems [2, 3].

Lanthanum strontium cobalt ferrite (LSCF), especially the composition  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  has multifunctional applications [4-6]. It is worth mentioning that, LSCF compounds as a cathode material for SOFCs shows high thermal and chemical stability, high mixed electronic-ionic conductivity and high compatibility with other fuel cell materials.

Different methods of synthesis such as solid-state reaction, co-precipitation, citrate gel, sol-gel, pyrolysis, combustion, gel-casting and pechini method have been employed for preparation of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  powders [7-9]. Conventional solid-state reaction route requires high calcination temperatures and long annealing times; which often results in agglomerated coarse particles and subsequent difficulty for achieving uniform distribution of particles for particular applications such as SOFCs cathodes. While, chemical routes often result in almost pure phase with uniform distribution and high surface area without any subsequent grinding in comparison to solid-state reaction routes. Among the chemical routes, co-precipitation is an appropriate method for synthesizing LSCF perovskite phase which can lead to obtaining ultrafine particles with uniform distribution [10]. Meanwhile, the phase formation and final microstructure of particles are strongly dependent on various factors such as pH of solution, stirring rate, process temperature, washing process of precursor and calcination temperature [11]. It was even found that the rate of addition of precipitating agent could have a significant effect on the shape and size of the final powders [12].

Nano-sized LSCF can be of much interest due to the strong influence of small particle size on improvement of the surface area and catalysis kinetic, in energy conversion systems such as the intermediate temperature SOFCs [13]. Although some researchers reported the synthesis of LSCF by co-precipitation route, it seems that there is lack of enough effort for optimizing the synthesis procedure. Successful

synthesis of LSCF by co-precipitation route was reported by Richardson et al. [7], however the effects of calcination temperatures on the phase formation of LSCF perovskite were not systematically investigated.

In this study, single phase  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  was successfully synthesized by a simple co-precipitation method. The effects of precipitating agent, repeatedly washing process of precursors and calcination temperature were systematically investigated. Specifications of selected samples were also compared with a commercial LSCF powder, with the aim of declaring that co-precipitation method has good ability to control the morphology of powders.

## 2. Experimental Procedure

Lanthanum strontium cobalt ferrite compound was synthesized by co-precipitation route using high purity analytical grade metal nitrates. In a typical experiment,  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Merck, >96%),  $\text{Sr}(\text{NO}_3)_2$  (BDH, >99%),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck, >99%) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (BDH, >99%) were dissolved in distilled water with stoichiometric ratio of 3:2:1:4 corresponding to the  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  compound. The pH of nitrate solutions was between 2-3, similar to the value reported by Toprak et al. [14]. Adjustment of pH was carried out by dropwise addition of precipitants into the above solution during magnetic stirring. Sodium hydroxide (NaOH, Merck, >99%) with  $\text{OH}^-/\text{NO}_3^-$  molar ratios of 1 and 2, and also ammonium carbonate ( $\text{CH}_6\text{N}_2\text{O}_2 \cdot \text{CH}_5\text{NO}_3$ , Merck) with a  $\text{NH}_4^+/\text{NO}_3^-$  molar ratio of 2 were added to the nitrate solution at the rate of 3 ml/min. In order to study the influence of washing process of precursor on the phase formation of final products, a sample was washed just once by distilled water at RT, while another sample was washed four times by distilled water at 70°C, followed by ethanol washing. All samples were dried at 80°C for 18h. Dried precursors were then calcined at various temperatures for 1h in air at a heating rate of 10°C/min. Figure 1 shows a schematic diagram of synthesis procedure in this study.

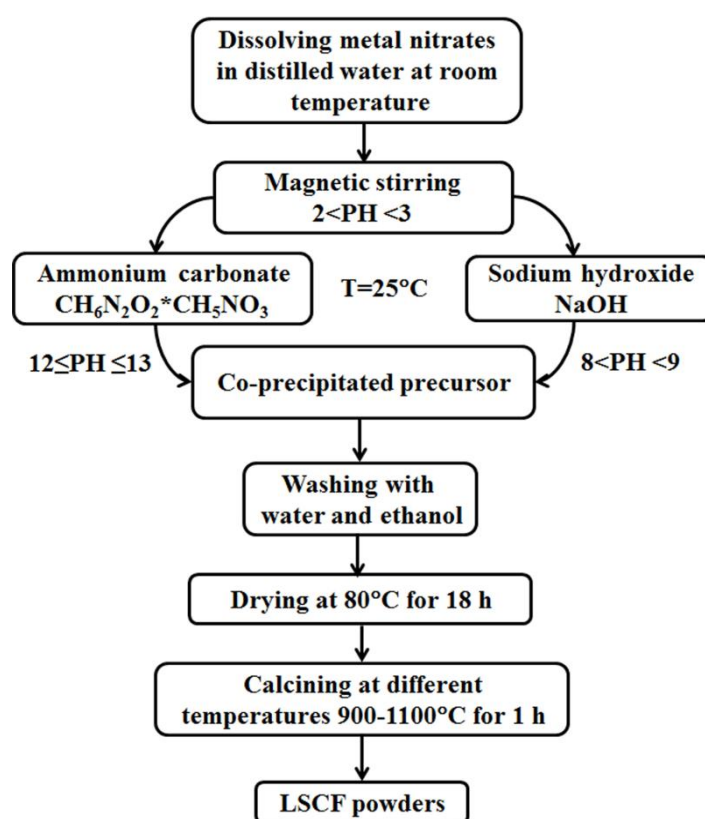


Fig. 1. Schematic procedure for synthesis of LSCF powders via co-precipitation route employed in this research.

The phase formation was studied by X-ray diffraction (XRD) technique at room temperature using Philips PW-1730 with Cu  $K_{\alpha}$  radiation ( $\lambda=1.5406 \text{ \AA}$ ) in the range of  $20 \leq 2\theta \leq 80$  and step size of 0.02. The mean crystallite size of the samples was calculated by Scherrer equation [15]:

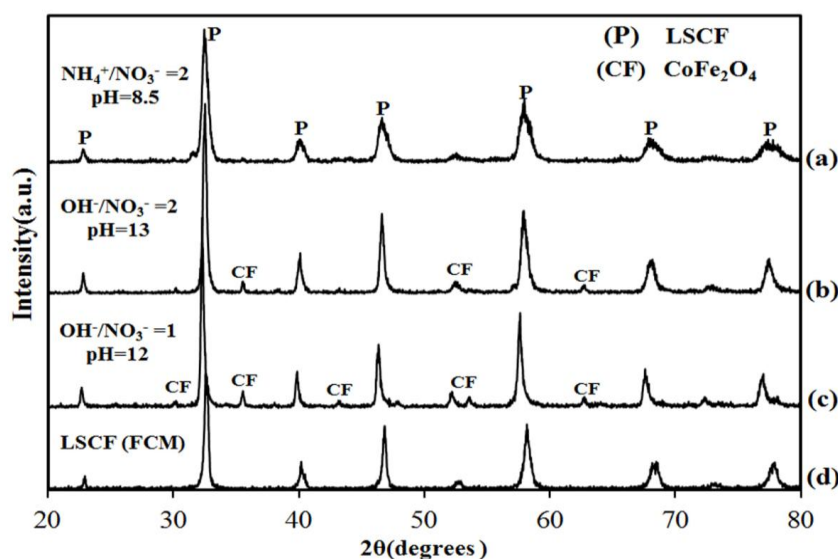
$$D = \frac{k \lambda}{\beta \cdot \cos \theta} \quad (1)$$

where  $K$  is a constant,  $\lambda$  is the wave length of Cu  $K_{\alpha}$  radiation, and  $\beta$  is the full width at half maxima of XRD peaks. The microstructure of the synthesized powders was observed by field emission scanning electron microscope (FESEM, TESCAN MIRA3). The mean particle size was calculated using MIP (Microstructure Image Processing) software measuring more than 20 particles from FESEM images. Commercial LSCF powder with similar composition was obtained from Fuel Cell Materials Co. (FCM, USA) for comparison of the specifications.

### 3. Results and Discussion

XRD patterns of synthesized powders after

calcination at  $1000^{\circ}\text{C}$  for 1 h are shown in Figure 2. It can be seen that both precursors co-precipitated by NaOH with  $\text{OH}^{-}/\text{NO}_3^{-}$  in a molar ratio of 1 and 2, contain some undesired secondary phases after calcination treatment, while co-precipitated samples with ammonium carbonate shows pure perovskite phase, similar to the XRD pattern of commercial LSCF powder (Figs. 2a and d). The ammonium carbonate co-precipitated powder was obtained at a pH value of 8.5, which is significantly lower than those of the other co-precipitated samples by NaOH which are equal to 12 and 13 (Figs. 2b and c). It is reported that for each particular method for synthesizing LSCF powder, there is an optimum pH range in which a high quality perovskite phase can be obtained [16-18]. It is worth mentioning that carbonates family of the precipitants provides higher stability of pH in metal nitrate solutions as well as higher homogeneity of solution. Furthermore, precipitation by sodium carbonate or ammonium carbonate leads to a well crystalline single phase powder after calcination [7, 19].



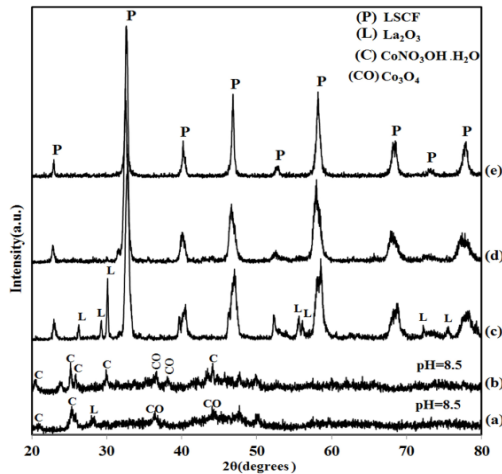
**Fig. 2.** The XRD patterns of calcined precursors processed by (a)  $\text{NH}_4^+/\text{NO}_3^- = 2$  (pH=8.5) (b)  $\text{OH}^-/\text{NO}_3^- = 2$  (pH=13) (c)  $\text{OH}^-/\text{NO}_3^- = 1$  (pH=12), all samples calcined 1 h at  $1000^\circ\text{C}$  and (d) commercial LSCF powder.

As indicated in Fig. 2, regardless of the  $\text{OH}^-/\text{NO}_3^-$  ratio, by employing NaOH as a precipitating agent, an undesired phase was observed on calcined samples as a minor phase. According to card No. JCPDS 02-1045, this secondary phase is related to cobalt ferrite oxide ( $\text{CoFe}_2\text{O}_4$ ) [20]. Rashad et al. [19] also found that co-precipitation of LSCF by NaOH can lead to a mixed phase product. It has been reported that chemical co-precipitation of precursors using precipitants containing hydroxide ions ( $\text{OH}^-$ ) usually consist of micron/submicron agglomerates of amorphous hydroxide or oxide-hydroxide nanoparticles [21]. Additionally, precipitants containing hydroxide ion ( $\text{OH}^-$ ) such as NaOH, KOH,  $\text{NH}_4\text{OH}$  can lead to a deficiency of strontium in the final powders due to the slight solubility of strontium hydroxide [22]. Whereas, precipitants belonging to the carbonates family can yield pure perovskite phase with desired composition and no cation deficiency [7].

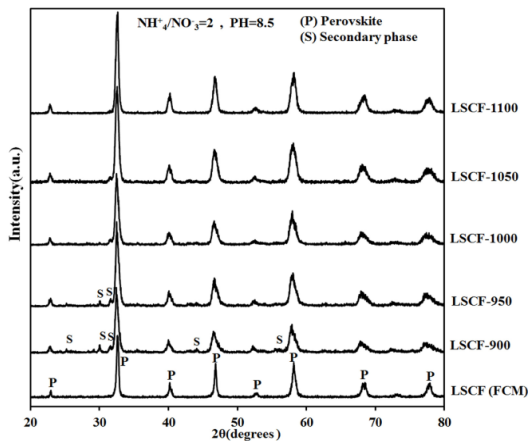
Figure 3 shows X-ray diffraction patterns for ammonium carbonate co-precipitated LSCF powder before and after calcination under various washing process. Curves designated by (a) and (b) are indicative of amorphous precursors and show some weakly crystallized structure of cobalt containing compounds. XRD patterns of calcined samples marked by (c) for easy washing and (d) for rigorous washing process revealed the remarkable effect of rigorous washing process on the elimination of

undesired secondary phases. The peaks in Figure 3c illustrates that washing the precursors by water and ethanol at RT (denoted as “1W25°C, 1Et”) was not able to remove undesired compounds and the XRD pattern shows  $\text{La}_2\text{O}_3$  peaks in final product. While, four times washing using water at  $70^\circ\text{C}$  followed by ethanol washing (denoted as “4W70°C, 1Et”) leads to a high purity phase. This phenomenon could be explained by higher ability of rigorous washing process to remove excessive salts and compounds from precursor. Obtaining mixed phases in a co-precipitation synthesis process was earlier reported by Rashad et al. [19], where they found  $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  through precipitation by NaOH (pH<10) after calcination at  $1000^\circ\text{C}$  for 2 h.

Figure 4 demonstrates X-ray diffraction patterns of powders co-precipitated by ammonium carbonate with a  $\text{NH}_4^+/\text{NO}_3^-$  ratio of 2 after calcining at different temperatures in the range of  $900$ – $1100^\circ\text{C}$ . XRD results revealed that, at calcination temperatures lower than  $1000^\circ\text{C}$  some minor secondary phases are presented and formation of perovskite phase is not complete, while at a temperature of  $1000^\circ\text{C}$  a single phase crystalline LSCF perovskite is formed. Further increase of calcination temperatures to  $1100^\circ\text{C}$  also increased the crystallinity of the powders.

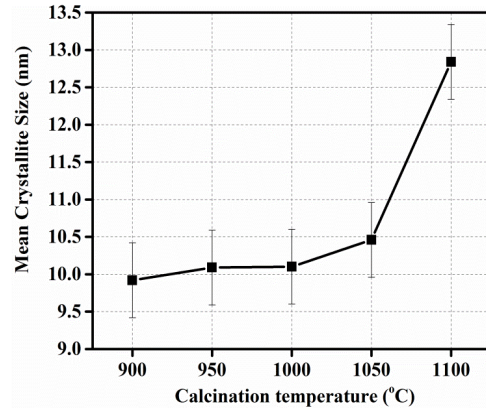


**Fig. 3.** XRD patterns of precursors (a) washed by “1W25°C,1Et”, (b) washed by “4W70°C,1Et” both dried for 18 h at 80°C, (c) and (d) calcined precursors corresponding to (a) and (b) at 1000°C for 1 h (e) commercial LSCF powder.



**Fig. 4.** XRD patterns of calcined co-precipitated precursor using  $\text{NH}_4^+/\text{NO}_3^-=2$  at  $\text{pH}=8.5$  after calcination at different temperatures in the range of 900-1100°C.

Temperature dependence of mean crystallite size for co-precipitated precursors with a  $\text{NH}_4^+/\text{NO}_3^-$  ratio of 2 after calcination at different temperatures is shown in Figure 5. It can be seen that by increasing calcination temperature from 900 to 1050°C, the mean crystallite size of LSCF powders remains almost constant in the range of 10 to 10.5 nm. However, increasing the calcination temperature to 1100°C rapidly increases the mean crystallite size by about 30%. The mean crystallite size of commercial LSCF powder was calculated using XRD pattern (LSCF-FCM sample in Fig. 4) and the corresponding value was around 19 nm.



**Fig. 5.** Mean crystallite size of co-precipitated precursor using  $\text{NH}_4^+/\text{NO}_3^-=2$  after calcination at different temperatures in the range of 900-1100°C.

FESEM micrographs of commercial LSCF powder as well as synthesized powders which were calcined at 1000 and 1100°C are presented in Figure 6. The presence of plate like particles in the commercial powder of Fig. 6a might be due to a final mechanical milling process on the powders. It can be seen that hard agglomerated semi-spherical nanoparticles with mean particle size of 90 and 130 nm were observed in LSCF-1000 and LSCF-1100 samples, respectively. Increasing calcination temperature from 1000 to 1100°C led to the intensive local sintering of LSCF powders. Indeed each agglomerated particle consist of several particle (or crystallite) as indicated by arrows in Figure 6(b). It can clearly be seen in Figure 6(c) that sever agglomeration has occurred in LSCF-1100 sample. These data show that 1100°C is a high calcination temperature and could not be an appropriate temperature for obtaining fine and discrete LSCF particles with uniform distribution. Table 1 illustrates a comparison of mean crystallite and particle size between LSCF powders prepared in this work with those earlier reported. As indicated, by employing a solid-state reaction process, it is difficult to obtain submicron particles with a uniform distribution, while chemical routes can lead to nano-sized particles. Based on the data in Table 1, specifications of co-precipitated powders in the present study are well comparable with those synthesized by other chemical routes. It is worth mentioning that, although the calcination temperature of the present study is relatively high compare to those earlier reported, the size and morphology of particles are comparable with others results.

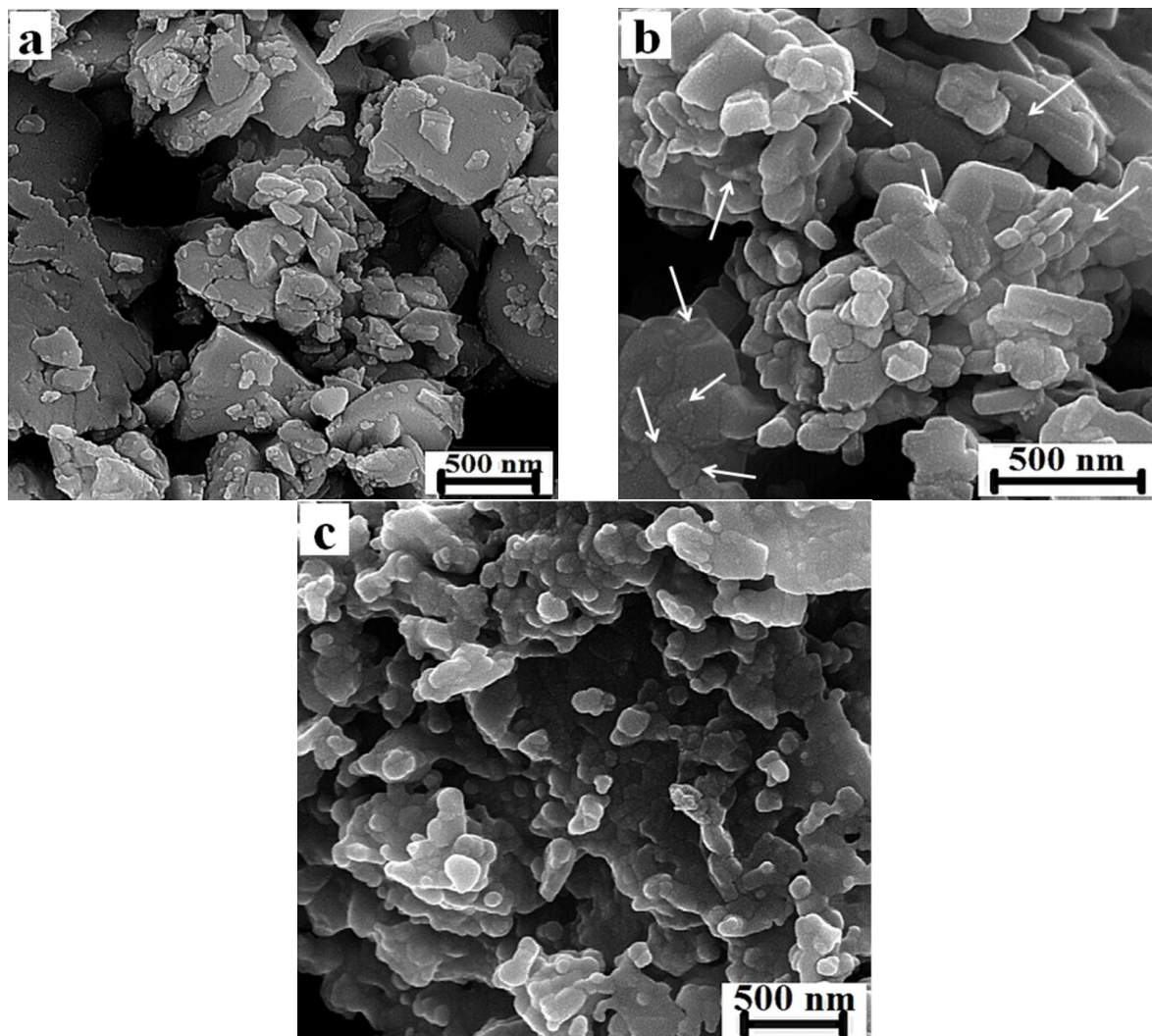


Fig. 6. FESEM micrographs of (a) commercial LSCF powder and LSCF powders synthesized by co-precipitation route using ammonium carbonate as precipitant with  $\text{NH}_4^+/\text{NO}_3^-=2$  after calcination at (b) 1000°C and (c) 1100°C.

Table 1. Comparison of calcination temperature, mean crystallite and particle size of LSCF powders prepared by various methods

Synthesis method of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF)	Calcination temperature (°C)	Mean crystallite size (nm)	Mean particle size (nm) FESEM	Reference
Co-precipitation	1000	10	90	Current work
Co-precipitation	1100	13	130	Current work
LSCF-FCM	-	19	280	FCM company
EDTA-citrate	600	14	-	[16]
Combustion	825	23	50	[8]
Gel-casting	950	-	124	[9]
Citrate-gel	900	-	70	[9]
Citrate-method	850	-	100	[23]
Co-precipitation	1000	-	>200	[7]
Mixed nitrate solid-state	1000	-	>2 $\mu\text{m}$	[7]
Pechini method	1000	-	>1 $\mu\text{m}$	[24]

#### 4. Conclusion

Nano-sized particles of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  was successfully synthesized via co-precipitation method using metal nitrates as starting materials and ammonium carbonate as precipitating agent at a relatively low pH value of 8.5. XRD analysis showed that applying rigorous washing of co-precipitated precursors before calcination led to enhanced purity of LSCF phase. A mixture of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  and  $\text{La}_2\text{O}_3$  was observed when precursor was simply washed by distilled water at RT. The mean crystallite size of the obtained LSCF powders processed by ammonium carbonate ( $\text{NH}_4^+/\text{NO}_3^- = 2$ ) after calcination at different temperatures of 900 to 1100°C were calculated in the range of 10 to 13 nm. FESEM micrographs revealed uniform distribution of ultrafine LSCF particles with mean particle size of 90 nm for the powders calcined at 1000°C for 1 h.

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