Synthesis and Characterization of Sr-doped LaFeO$_3$ perovskite by sol-gel auto-combustion method

M Kaewpanha$^{1,*}$, T Suriwong$^{1,*}$, W Wamae$^2$ and P Nunocha$^1$

$^1$ School of Renewable Energy and Smart Grid Technology, Naresuan University, Phitsanulok 65000, Thailand
$^2$ Renewable Energy Technology Department, Faculty of Science Technology and Agriculture, Yala Rajabhat University, Yala 95000, Thailand

*Corresponding author: malineek@nu.ac.th, tawats@nu.ac.th

Abstract. In the present study, La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.0, 0.2, 0.4, 0.6$ and $0.8$) perovskite was successfully prepared by sol-gel auto-combustion method. The prepared samples were characterized by X-ray diffraction (XRD), Field-emission scanning electron microscope (FESEM) with energy dispersive spectrum (EDS), Fourier transform infrared spectroscopy (FTIR) and spectrofluorometer. XRD and FESEM show that the prepared Sr-doped LaFeO$_3$ is single phase perovskite and nanosize with relatively homogeneous particle size distribution. Moreover, FESEM-EDS mapping analysis also exhibits the uniform distribution of all elements. The effect of Sr content in LaFeO$_3$ on the structure and morphology was also investigated. As results, the increasing of Sr content only affects the Fe-O stretching mode of LaFeO$_3$ perovskite, while it has little effect on the particle size and morphology of the Sr-doped LaFeO$_3$.

1. Introduction

Perovskite-type oxides of general formula ABO$_3$ (A = rare or alkali earth metals, B = transition metals) have become one of the most promising candidates due to their wide range of physical and technological properties, such as ferroelectricity, piezoelectricity, pyroelectricity, high-temperature superconductivity, magnetic behavior, and catalytic activity [1]. These properties determine the use of such materials in many applications such as gas transducers, catalysts, solid electrolyte batteries and magnetic sensors [2]. Among perovskite-type oxides, LaFeO$_3$ (LFO) is of interest because of its low price, non-toxicity, abundant reserve, and excellent electrochemical capacity [3]. Moreover, doping LaFeO$_3$ with divalent metal at A-site and transition metals at B-site affects its structural, transport, and electrical properties [3-5].

There are several methods for the synthesis of perovskite-type oxide LaFeO$_3$ such as solid-state reaction, sol-gel method, co-precipitation, and hydrothermal process [6-10]. Although solid-state reaction is the most common preparation method for LaFeO$_3$ powder, the synthesis occurs at high temperature (>1000 °C), resulting in powder products of non-porous, irregular shape, uncontrolled particle size and low surface area [7, 11]. Alternative methods to solid-state reaction methods such as sol-gel method, co-precipitation, and hydrothermal process, etc. have been reported to synthesize materials with better control of particle size and morphology [6, 8-10]. In addition, sol-gel auto-combustion is widely used for the preparation of inorganic ceramic and composite materials, with controlled properties for several applications [12, 13]. This is a novel way with a combination of the chemical sol–gel process and the combustion process. The advantages of sol–gel auto-combustion...
include: inexpensive precursors; a simple preparation method; and a resulting nano-sized, homogeneous, highly reactive powder [14]. Therefore, the sol-gel auto combustion method has been considered as an attractive and quality technique for the preparation of oxide materials. However, no such reports have been found in literature on the synthesis of undoped and Sr-doped LaFeO$_3$ (LSF) materials by the sol-gel auto-combustion method.

In this work, therefore, we focus on the synthesis of undoped and Sr-doped LaFeO$_3$ (LSF) by sol-gel auto-combustion method. The synthesized LSF powder also were characterized by XRD, FESEM-EDS, FTIR and spectrophotometer.

2. Experimental

2.1 Materials

Analytical grade lanthanum nitrate hexahydrate (La(NO$_3$)$_3$·6H$_2$O, Lobachemie, India), iron nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O, Lobachemie, India), strontium nitrate (Sr(NO$_3$)$_2$, Himedia, India), citric acid (C$_6$H$_8$O$_7$, Lobachemie, India), and ethylene glycol (C$_2$H$_6$O$_2$, Lobachemie, India) were used as reagents for synthesis.

2.2 Synthesis of LSF powders

In this work, La$_{1-x}$Sr$_x$FeO$_3$ with $x = 0.0, 0.2, 0.4, 0.6, 0.8$, were prepared by the sol-gel auto-combustion method. Firstly, lanthanum nitrate hexahydrate, strontium nitrate and iron nitrate nonahydrate were weighted in stoichiometric proportions and were dissolved in distilled water by a magnetic stirrer. Subsequently, when the metal salts were completely dissolved in the solution, citric acid was added to the precursor solution. The molar amount of citric acid was equal to a total molar amount of metal nitrates in the solution. This solution was heated to $80 \, ^\circ C$ on a heating plate with stirring for 2 hours using a magnetic stirrer, followed by the addition of ethylene glycol in a molar ratio of citric acid:ethylene glycol of 1: 4. Then, the solution was further heated to $110 \, ^\circ C$ to achieve the gel formation. For the auto-combustion step, the gel formation was put rapidly into electrical oven at temperature of $180 \, ^\circ C$ for 1 hour to obtain foamy dry powders, known as as-synthesized powders. These powders were grinded and calcined at the temperature of $900 \, ^\circ C$ for 2 hours in a muffle furnace to make the incompletely combusted part react thoroughly. The LSF powders were finally obtained.

2.3 Characterization

The phase and crystallinity of LSF powders were determined by powder X-ray diffraction (XRD) using a Philips X’Pert PANalytical X-ray diffractometer with Cu-K$_\alpha$ radiation ($\lambda = 1.540598 \, \text{Å}$) over Bragg’s angles ($2\theta$) ($10^\circ \leq 2\theta \leq 80^\circ$) at a step size of 0.02 and time/step of 1 s. The average crystallite size (D) of the samples was estimated using Scherrer’s formula:

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

where $K$ is the shape factor of the average grain size (the expected shape factor is 0.89), $\lambda$ is the characteristic wavelength ($\lambda = 1.540598 \, \text{Å}$) and $\beta$ is the full width at half maximum of the X-ray peak. Field-emission scanning electron microscope (FESEM, JEOL JSM-6335F) with energy dispersive spectrum (EDS) facility was employed to study the microstructure characteristics of the LSF powders. The fourier transform infrared spectra (FTIR) were recorded using a Thermo Scientific Nicolet 6700 FTIR spectrometer. The photoluminescence (PL) property of the LSF powders was investigated by a fluoromax 4 spectrophotometer using excitation wavelength ($\lambda_{ex}$) of 310 nm at room temperature.
3. Results and discussion

Fig. 1 presents the XRD patterns of La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.0, 0.2, 0.4, 0.6$ and $0.8$) samples calcined at $900 \, ^\circ\text{C}$ in the air atmosphere, compared with the JCPDS database No. 37–1493 and 40-0905 for LaFeO$_3$ and SrFeO$_{2.97}$ phases, respectively [15]. It was found that the main diffraction peaks of all samples are indexed according to the LaFeO$_3$ phase, indicating the single perovskite phase with an orthorhombic structure and no evidence of any impurity phases (Fig.1a). The Sr-doping up to 80% does not significantly affect the crystal structure of LaFeO$_3$. Fig. 1b shows the magnified XRD patterns of all the samples at the 2$\theta$ range between 30$^\circ$ and 35$^\circ$ including the reflection of the (121) plane. It is observed that the (121) peak is a significant shifting toward higher 2$\theta$ angle with increasing the amount of Sr dopant, which can be attributed to the lattice structure distortion induced by Sr doping [16, 17]. This is due to the substitution of the larger atomic radius of La (1.15 Å) by the smaller atomic radius of Sr (1.13 Å) [16, 18].

![Figure 1. XRD patterns of the samples of La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.0, 0.2, 0.4, 0.6$ and $0.8$).](image)

The average crystallite size ($D$) of undoped and Sr-doped LaFeO$_3$ samples are summarized in Table 1. It can be seen that there is no significant difference in average crystallite size of the samples. The average crystallite size of undoped LaFeO$_3$ was found to be 37 nm, while the average crystallite size of Sr-doped LaFeO$_3$ was found to be 30.1, 32.5, 34.7 and 37.5 when $x = 0.2, 0.4, 0.6$ and 0.8 nm, respectively. The present average crystallite size of all the powders relatively close to those of the
undoped and doped LaFeO$_3$ prepared by sol-gel method [6, 17, 19]. So, undoped and Sr-doped LaFeO$_3$ perovskite powder have been successfully synthesized through sol-gel auto-combustion method.

### Table 1. Crystallite size and particle size of the La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.0, 0.2, 0.4, 0.6$ and $0.8$) samples.

| Samples           | Crystallite Size (nm) | Particle Size (nm) |
|-------------------|-----------------------|-------------------|
| LaFeO$_3$         | 37.9                  | 264               |
| La$_{0.8}$Sr$_{0.2}$FeO$_3$ | 30.1              | 153               |
| La$_{0.6}$Sr$_{0.4}$FeO$_3$ | 32.5              | 222               |
| La$_{0.4}$Sr$_{0.6}$FeO$_3$ | 34.7              | 212               |
| La$_{0.2}$Sr$_{0.8}$FeO$_3$ | 37.5              | 238               |

To further ascertain the presence of LSF, FTIR technique was employed to obtain information about the chemical bonding in the material. The FTIR spectra of undoped and Sr-doped LaFeO$_3$ powders are shown in Fig. 2. The results exhibit relatively differences at the absorption peaks of 536 cm$^{-1}$ which referred to Fe-O stretching vibration mode [6, 17]. The disappearance of the characteristic bands of Fe-O stretching mode of LSF with the increasing of Sr content revealed that the substitution of Sr in LaFeO$_3$ has a significant effect to Fe-O stretching vibration mode. However, Sr-O stretching mode at 864 and 859 cm$^{-1}$ was not detected in all the LSF samples, compared to the LaFeO$_3$ and La$_{0.7}$Sr$_{0.3}$FeO$_3$ samples [17]. Moreover, there was no observation of absorption peaks at about 1300 and 1600 cm$^{-1}$ which referred to carboxyl group and NO$_3^-$ stretching mode, indicating that all the carboxyl group and the NO$_3^-$ ion took part completely in the reaction during combustion.

![Figure 2. FTIR spectra of La$_{1-x}$Sr$_x$FeO$_3$ ($x = 0.0, 0.2, 0.4, 0.6$ and $0.8$) samples.](image)

The morphology of LSF perovskite particles evaluated by FESEM is shown in Fig. 3. It can be observed that all the synthesized LSF powders have an irregular shape with very uniform particle size distribution and small amount of agglomerations of particles. The average particle size of all the samples is summarized in Table 1. The average particle size of undoped LaFeO$_3$ was found to be 264 nm, while the average particle size of Sr-doped LaFeO$_3$ was found to be 153, 222, 212 and 238 when $x = 0.2, 0.4,$


0.6 and 0.8 nm, respectively. The present morphology of LSF powder is quite similar to that synthesized by citrate sol-gel route [17]. This indicates that there is no significant difference in surface morphology and particle size of LSF powders with the increasing Sr dopant, corresponding to the XRD results.

Figure 3. FESEM images of \( \text{La}_{1-x}\text{Sr}_x\text{FeO}_3 \) \((x = 0.0, 0.2, 0.4, 0.6 \text{ and } 0.8)\) samples.

To consider the chemical distribution and composition of LSF samples, FESEM-EDS with mapping analysis techniques were used to characterize the samples. Fig. 4 shows typical FESEM-EDS mapping of \( \text{La}_{0.4}\text{Sr}_{0.6}\text{FeO}_3 \) sample. The EDS mapping revealed that the sample consisted of detected La, Sr, Fe and O elements with relatively uniform distribution on the sample surface. The quantitative EDS analysis confirmed that the chemical composition was in good agreement with stoichiometric chemical
composition, as shown in Table 2. As for the other samples, similar results to those for La$_{0.4}$Sr$_{0.6}$FeO$_3$ sample were obtained.

**Figure 4.** FESEM and EDS mapping images of La$_{0.4}$Sr$_{0.6}$FeO$_3$ sample.
Table 2. Elemental atomic composition of LSF samples through the EDS analysis.

| Samples         | Atomic (at.%) |
|-----------------|---------------|
|                 | La     | Sr     | Fe     | O      |
| LaFeO₃          | 24.68  | 0.00   | 22.45  | 52.80  |
| La₀.₈Sr₀.₂FeO₃  | 17.10  | 4.55   | 20.23  | 58.13  |
| La₀.₆Sr₀.₄FeO₃  | 15.41  | 9.35   | 21.82  | 53.42  |
| La₀.₄Sr₀.₆FeO₃  | 9.15   | 14.28  | 20.13  | 56.44  |
| La₀.₂Sr₀.₈FeO₃  | 4.58   | 18.26  | 20.41  | 56.74  |

Figure 5. Photoluminescence spectra of La₁₋ₓSrₓFeO₃ (x=0.0, 0.2, 0.4, 0.6 and 0.8) samples.

To understand the diffusion and the recombination rate of photogenerated electron–hole pairs, PL spectroscopy was investigated. Generally, PL intensity is related to the recombination rate of electron–hole pairs. The low PL intensity implies the low recombination rate and the high separation rate of photogenerated carriers, resulting in the high photocatalytic activity under light irradiation. PL spectra of the as-synthesized La₁₋ₓSrₓFeO₃ (x=0.0, 0.2, 0.4, 0.6 and 0.8) particles excited at 310 nm wavelength are shown in Fig. 5. Undoped LaFeO₃ powder shows the emission peaks at around 380 and 560 nm. However, all the LSF powders show only the highest emission peaks at around 380 nm. The emission peak of the LSF samples disappeared at 560 nm probably due to a higher photocatalytic activity under light irradiation as results of Sr dopant [20].

4. Conclusions
In the present study, the undoped and Sr-doped LaFeO₃ (LSF) perovskite has been successfully synthesized by new route sol-gel auto-combustion method. XRD and FESEM results showed that the as-prepared LSF samples were single phase with no detection impurities and uniform size distribution. The Sr-doping up to 80% does not significantly affect the crystal structure and particle size of LSF. The FESEM-EDS mapping analysis showed that all samples consisted of detected La, Sr, Fe and O elements with relatively uniform distribution on the sample surfaces. In addition, the chemical composition of the
samples corresponded to stoichiometric chemical composition. The FTIR spectra revealed that the substitution of Sr in LaFeO$_3$ has a significant effect to Fe-O stretching vibration mode.

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