Temperature-dependent impedance spectroscopy of La$_{0.8}$Sr$_{0.2}$FeO$_3$ nano-crystalline material

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Abstract. LaFeO$_3$ is a material with perovskite structure which electrical properties frequently investigated. Research are done due to the exhibition of excellent gas sensing behavior through resistivity comparison from the p-type semiconductor. Sr doping on LaFeO$_3$ or La$_{1-x}$Sr$_x$FeO$_3$ are able to improve the electrical conductivity through structural modification. Using Sr dopant concentration (x) of 0.2, La$_{0.8}$Sr$_{0.2}$FeO$_3$ nano-crystal pellet was synthesized. The synthesis used sol-gel method, followed by gradual heat treatment and uniaxial compaction. XRD characterization shows that the structure of the sample is Orthorhombic Perovskite. Topography of the sample by SEM reveals grain and grain boundary existence with emerging agglomeration. The electrical properties of the material, as functions of temperature and frequency, were measured by Impedance Spectroscopy method using RLC meter, for temperatures of 303-373K. Through the Nyquist plot and Bode plot, the electrical conductivity of La$_{0.8}$Sr$_{0.2}$FeO$_3$ is contributed by the grain and grain boundary. Finally, the electrical permittivities of La$_{0.8}$Sr$_{0.2}$FeO$_3$ are increasing with temperature increase, with the highest achieved when measured at 1 kHz frequency.

1. Introduction
The synthesized perovskite LaFeO$_3$ is often applied as an electrode material for Solid Oxide Fuel Cells (SOFC), and electrocatalytic material as in gas sensors [1, 2]. However, there are possibilities that the compound is able to increase its mediocre electrical conductivity by the giving of doping [3]. Sr$^{2+}$ cation is one well-known doping for increasing LaFeO$_3$ electrical conductivity, by generating oxygen vacancies $\delta$ that increasing O$^{2-}$ ion mobility, and/ or causing the Fe cation oxidized from Fe$^{3+}$ to Fe$^{4+}$ [3, 4]. The size and oxidation numbers of Sr$^{2+}$ cation doping towards LaFeO$_3$ perovskite would affect its electrocatalytic behavior, however these values are adjustable by doping composition calculation to achieve the desirable certain degree.

The composition of La$_{0.8}$Sr$_{0.2}$FeO$_3$ from the La$_{1-x}$Sr$_x$FeO$_3$ group is usually used as the electrode for fuel cells. This is due to its superior electrochemical behavior compared with the other members of the set, even though it did not have the most oxygen vacancies $\delta$ [5, 6]. The very small deviation from this composition, La$_{0.75}$Sr$_{0.25}$FeO$_3$ is reported to have the excellence on “syngas” (synthesis gas, mainly consist of H$_2$, CO, and CO$_2$) production (hence energy production) through catalytic partial oxidation from methane (CH$_4$), due to its relatively wide BET (Brunauer – Emmett – Teller) surface area and its relatively plentiful H$_2$ reduction agent consumption [7].

From previous backgrounds, this work focuses on the study of electrical behavior of nano crystalline La$_{0.8}$Sr$_{0.2}$FeO$_3$ by using Impedance Spectroscopy (IS) method. The data acquisition through different
system temperatures, enables the possibility to calculate the activation energy for relaxation and conduction processes.

2. Materials and methods

The material is synthesized using sol-gel method, with citric acid and aquadest as chelating agents. For synthesizing La$_{0.8}$Sr$_{0.2}$FeO$_3$, each 30 mmol of (0.4 ×) La$_2$O$_3$, (0.2 ×) Sr(NO$_3$)$_2$, and Fe(NO$_3$)$_3$.9H$_2$O were mixed with the chelating agents in a beaker glass. Then, the colloid phase sample was heated and stirred on a Magnetic stirrer – Hot plate (WiseStir MSH-20D), with temperature of 120°C and rotational speed of 700 rpm. After the sample transform into the gel phase, it experienced gradual heat treatments (200°C for 5 h, 900°C for 6 h). Finally, the resulting powder was pressed into pellet with pressure of 5 ton/ square inch for 120 s and then sintered at 1300°C for 1 h.

The XRD characterizations of the calcined powder and the sintered pellet were done on room temperature, by Rigaku MiniFlex 600 X-Ray Diffractometer with radiation source of Cu Kα (λ = 1.5418 Å), with the 2θ range from 5° to 90°. The topography of the sample were investigated by SEM, using JEOL JSM-6510 LA electron microscope with acceleration voltage of 20 kV and magnification of 50000 ×. For the Impedance Spectroscopy (IS) characterization, the pellet was modelled as parallel plate capacitor, connected with conductor probe, and inserted on a thermocouple furnace that was connected to a Fluke PM6306 RLC meter. The measurements were done between temperature 303-373K and frequencies 1 MHz, 100 kHz, 10 kHz, and 1 kHz.

3. Results and discussion

Figure 1 shows the XRD pattern of the La$_{0.8}$Sr$_{0.2}$FeO$_3$ sample, both on the calcined powder phase and sintered pellet phase. The XRD pattern reveals that La$_{0.8}$Sr$_{0.2}$FeO$_3$ have Orthorhombic perovskite structure and space group Pnma. There are no other phases observed in the samples, indicating that the samples are single phase.

Table 1 lists the measured structure identities of the La$_{0.8}$Sr$_{0.2}$FeO$_3$ sintered pellet. Its grain size was calculated using Scherrer equation (equation 1) [8], and its tolerance factor follows Goldschmidt equation (equation 2) [9].

\[
\tau = \frac{K\lambda}{B \cos \theta}
\] (1)

On equation (1), \(K\) is the shape factor usually values 0.9, \(\lambda\) is the used X-ray wavelength, \(B\) is the Full Width at Half Maximum (FWHM) of the selected peak on radian, and \(\theta\) is the Bragg angle. As an approach, Scherrer equation may gives different crystallite size value, compared with the electron microscope characterization, if the tested crystal experienced inhomogeneous strain and crystal defect.

\[
\tau = \frac{r_A + r_O}{2^{1/2}(r_B + r_O)}
\] (2)

On equation (2), \(r_A\), \(r_B\), and \(r_O\) are the ionic radius of A-site cation, B-site cation, and oxygen anion, respectively. The less the tolerance factor value from unity, the lower the crystal structure regularity level of the perovskite.

Figure 2 shows the atomic position manifestation on the La$_{0.8}$Sr$_{0.2}$FeO$_3$ lattice, and table 2 lists the unit cell position of the related elements. Both information reveal that the Sr$^{2+}$ doping composition still not showing a significant Fe oxidation from Fe$^{3+}$ to Fe$^{4+}$, and the variation occurs only on the comparison of the number of A-sites atoms (Sr and La).

Figure 3 shows the SEM image of La$_{0.8}$Sr$_{0.2}$FeO$_3$. The SEM image shows that the grain distribution of the sample is uniform and quite good, with some grain agglomeration observed. There are no obvious signs of secondary phases observed on the image. Using the measuring bar included in the image, La$_{0.8}$Sr$_{0.2}$FeO$_3$ had the grain size of about 0.167 µm, with agglomeration size of about 0.333 µm. This agglomeration condition makes it rather hard to distinguish between its grain and its grain boundaries, indicating that the contribution of the grain boundary in measured impedance would show inhomogeneous values, compared with the grain contribution.

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Figure 1. XRD pattern of La$_{0.8}$Sr$_{0.2}$FeO$_3$ showing single phase orthorhombic perovskite crystal structure with Pnma space group.

Table 1. Structure identities of the La$_{0.8}$Sr$_{0.2}$FeO$_3$ sintered pellet.

| Identity | a (Å) | b (Å) | c (Å) | Crystallite size (nm) | Density (g/cm$^3$) | Tolerance factor |
|----------|-------|-------|-------|-----------------------|-------------------|-----------------|
| Value    | 5.555 | 7.855 | 5.514 | 23                    | 6.42              | 0.893           |

Table 2. Unit cell position of the related elements in La$_{0.8}$Sr$_{0.2}$FeO$_3$.

| Elements | Sr    | La    | Fe    | O1    | O2    |
|----------|-------|-------|-------|-------|-------|
| x        | 0.4724| 0.4724| 0.0000| 0.2290| 0.5060|
| y        | 0.2500| 0.2500| 0.0000| 0.0350| 0.2500|
| z        | 0.0010| 0.0010| 0.0000| 0.2660| 0.5700|

Oxidation numbers +2 +3 +3 -2 -2

Figure 2. Atomic position on La$_{0.8}$Sr$_{0.2}$FeO$_3$ lattice.

Figure 3. SEM images of La$_{0.8}$Sr$_{0.2}$FeO$_3$ with the magnification of 50000 x.
Figure 4 shows the Nyquist plots of the La$_{0.8}$Sr$_{0.2}$FeO$_3$ sample on varying temperatures, from RT to 373 K. The Nyquist plot curves have the form of almost a semicircle, however the high-temperature curves have slightly additional shape on small Z' values (high frequencies), which resemble another semicircle that showing the influence of grain and grain boundaries on the electrical properties of the material. The lowering of temperatures would enlarge the radius of the Nyquist plot semicircles, showing that the impedance values are increasing. This temperature-dependence impedance phenomenon indicates that La$_{0.8}$Sr$_{0.2}$FeO$_3$, as a member of La$_{1-x}$Sr$_x$FeO$_3$, is a semiconductor [10]. The double semicircle Nyquist plots are fitted using ZSimpWin software, that aims to acquire the appropriate equivalent electronic circuits and the component values. The proposed equivalent electronic circuit as the electrical properties model is the (RC)(RC) circuit, where one (RC) part represents grain contribution and the another (RC) part represents grain boundary contribution. Using ZSimpWin software and the Nyquist plots, the component values of this equivalent electronic circuit has been obtained for each temperatures, written in table 3. It can be concluded that the multiplication of R and C (also known as relaxation time $\tau$) from grain contribution is having tendency to be smaller than the ones from grain boundary contributions. That means for the process of conduction in La$_{0.8}$Sr$_{0.2}$FeO$_3$, grain conduction is more reliable than the grain boundary conduction, probably due to agglomeration observed that blur the grain boundaries [11].

Figure 5 shows imaginary impedance $Z''$ ordinate Bode plots of the La$_{0.8}$Sr$_{0.2}$FeO$_3$ sample on varying temperatures, from RT to 373 K. The $Z''$ ordinate Bode plots show that along with frequency increase, the curve increasing until a certain maximum point, and then goes down. Those peaks reveal a distribution of relaxation time of conduction process, which is also temperature-dependence. The peak shift on the Bode plots shows that the relaxation time becoming faster with temperature increase [11]. This phenomenon happens because the peak frequencies on the plots are inversely proportional to the dielectric relaxation time, and increasing temperature caused the peak frequencies to increase.

After dealing with semiconducting behavior of La$_{0.8}$Sr$_{0.2}$FeO$_3$, next is the discussion about its dielectric behavior through the complex permittivity quantity $\varepsilon$. Real relative permittivity (dielectric constant $\varepsilon'$) represents its ability to store electrical energy, while imaginary relative permittivity (dielectric loss $\varepsilon''$) represents its ability to dissipate electrical energy. Figure 6 shows La$_{0.8}$Sr$_{0.2}$FeO$_3$ real permittivity curves toward the temperatures. The plot of real permittivity versus temperature, shows that the less the frequencies of data acquisition, the more the real permittivity values. Moreover, the real permittivity increase with temperature increase. Because both real and imaginary permittivities are inversely proportional to frequency, there is an assumption that the imaginary permittivity also follow the same trend [11].

| $T$ (K) | $R_1$ (Ω) | $C_1$ (F) | $R_2$ (Ω) | $C_2$ (F) |
|--------|-----------|-----------|-----------|-----------|
| 300    | 148.30    | 4.424x10^{-6} | 1.97      | 4.322x10^{-20} |
| 323    | 16.91     | 9.624x10^{-7}  | 105.90    | 4.680x10^{-9}  |
| 333    | 17.01     | 9.961x10^{-9}  | 87.24     | 4.977x10^{-7}  |
| 343    | 18.39     | 2.179x10^{-16} | 68.95     | 5.508x10^{-6}  |
| 353    | 20.64     | 1.000x10^{-20} | 51.48     | 6.485x10^{-6}  |
| 363    | 23.66     | 1.015x10^{-23} | 33.14     | 9.210x10^{-6}  |
| 373    | 1.77      | 1.795x10^{-6}  | 26.30     | 1.328x10^{-20} |
Figure 4. Nyquist plots of the La$_{0.8}$Sr$_{0.2}$FeO$_3$ sample on varying temperatures.

Figure 5. $Z''$ Ordinate bode plots of the La$_{0.8}$Sr$_{0.2}$FeO$_3$ sample on varying temperatures.
4. Conclusions
La$_{0.8}$Sr$_{0.2}$FeO$_3$ was successfully synthesized by sol-gel method. XRD results show single phase Orthorhombic Perovskite crystal structure with Pnma space group. SEM image shows that the synthesized product is uniform and quite good in grain distribution, with a few grain agglomeration observed. Impedance Spectroscopy characterization shows that in general, the sample had semiconducting behavior or impedance decrease with the increase of temperature. The electrical conductivity of La$_{0.8}$Sr$_{0.2}$FeO$_3$ is contributed by both grain and grain boundary, and the dielectric relaxation time of the sample is faster with increasing temperature.

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