Synthesis of superconductor La$_{1.84}$Sr$_{0.16}$CuO$_4$ with sol-gel method

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Abstract. In this work, we report structure, morphology, and chemical composition of La$_{1.84}$Sr$_{0.16}$CuO$_4$ which have been synthesized using the sol-gel method. X-ray diffraction (XRD) analysis shows that the sample stabilized in tetragonal structure with I4/mmm space group. Morphological analysis using Scanning Electron Microscope (SEM) shows that the average grain size of the sample is 155.13 nm. Furthermore, Electron Dispersive Spectroscopy (EDS) result confirmed the sample is composed with the appropriate elements, even though the result is different compared to calculated value using stoichiometric calculation.

1. Introduction
The interest in layered cuprate materials began when Bednorz and Muller discovered superconductivity in La$_{2-x}$Ba$_x$CuO$_4$ [1]. Since then, there are much research which dedicated to finding a better critical temperature ($T_c$) in layered cuprate materials. The most common method that was used in this field of study is to vary the hole concentration inside the sample by modifying the chemical composition of La$_{2-x}$Ba$_x$CuO$_4$ [2]. One of the most well-known layered cuprate superconductors is La$_{1-x}$Sr$_x$CuO$_4$ (LSCO). In single crystal form, LSCO can achieve critical temperature up to 42 K [3].

It becomes an interest to find an easy method which can form a single phase LSCO material in order to have high applicability in daily life. The sol-gel method is one of the most well-known methods to form a single phase ceramic compound. However, it is hard to find any research regarding layered cuprate which has been synthesized using the sol-gel method. Thus, using the sol-gel method is a novelty in which this method is relatively easier compared to solid state method which has been commonly used to synthesize LSCO material. Additionally, it is commonly known that the sol-gel method could produce a sample in the nanometric scale. Therefore, in this research LSCO sample with chemical formula La$_{1.84}$Sr$_{0.16}$CuO$_4$ will be synthesized using the sol-gel method. Moreover, the crystal structure of the sample will be examined using XRD. Additionally, Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) will be used to observe the microstructure of the sample and evaluate the purity of the sample subsequently.

2. Materials and Methods
The La$_{1.84}$Sr$_{0.16}$CuO$_4$ was synthesized using the sol-gel citrate-nitrate combustion method. The stoichiometric calculation of the precursor used is La$_2$O$_3$ (Merck 99.5%), Sr(NO$_3$)$_2$ (Merck, 99.5%), (Cu(NO$_3$)$_2$.3H$_2$O (Merck, 99.5%), and citric acid C$_6$H$_{12}$O$_7$.H$_2$O (Merck 99.5%). In this sol-gel method, are precursors must in metal nitrate form. First, La$_2$O$_3$ dilute by nitrate acid following chemical reaction:
La$_2$O$_3$ + 6HNO$_3$ $\rightarrow$ 2La(NO$_3$)$_3$ + 3H$_2$O

Each precursor was diluted to get a clear solution by the minimum amount of aquabidest water. After that, precursors were mixed to the beaker glass and added citric acid following as reaction:

$$1.84\text{La(NO}_3\text{)}_3 + 0.16\text{Sr(NO}_3\text{)}_2 + \text{Cu(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O} + \beta \text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O} \rightarrow \text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4 + \delta \text{N}_2 + \gamma \text{H}_2\text{O} + \alpha \text{CO}_2$$

Citric acid was added using ratio citric acid to metal ion as much as 1:1. In this sol-gel method, citric acid played a role as metal ions complexant and as fuel [5]. The structure of the sample was characterized at room temperature by X-ray diffraction (XRD). The morphology and composition of the powder samples investigated by scanning electron microscopy (SEM) and Electron Dispersion Energy (EDS).

3. Result and Discussion

Figure 1 shows the refined XRD pattern obtained from sample LSCO. Based on the figure, it can be seen that the obtained LSCO sample has not achieved a single phase state with a small additional phase. Based on the refinement process, this additional phase can address as a La$_2$O$_3$ phase which is the precursor that was used in this sol-gel method. The strongest reason behind this result can be caused by the lack of nitric acid that was used to convert lanthanum metal in oxide form into its nitrate form. According to the chemical reaction, in order to form a pure LSCO material with the desired compound, it is crucial to have all the lanthanum metal in nitrate form. Based on the refined XRD pattern, this additional phase is quite small (less than 5% of the sample volume fraction) thus, it is believed to not greatly affect the overall superconductivity of the sample.

![Figure 1. Results of Rietveld analysis of the XRD pattern LSCO](image)

The structural parameter obtained from Rietveld refinement process are listed in Table 1. Based on the result, it can be seen that different synthesis method can affect the lattice parameter of the sample. This result is significant because, in layered cuprate superconductor, the critical temperature of the sample is highly correlated with the crystallographic aspect of the sample, in particular, the bond length between copper and oxygen ions. Thus, based on the obtained result, it can be predicted that the LSCO sample made using sol-gel method will have a different critical temperature compared to the sample made by solid state method. The average crystallite size is calculated using Scherrer’s equation [6].
Figure 2 shows the SEM image of LSCO. Based on the micrographic method, it can be calculated that the average grain size is 155.13 nm. The obtained result from micrographic approach is more massive compared to the result obtained from crystallography approach using the Scherrer equation. This result suggests that one single grain which could be seen from SEM micrograph consists of several smaller crystallite (Table 1).

| Parameter               | \( \text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4 \) | \( \text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4 \) [4] |
|-------------------------|---------------------------------------------------|---------------------------------------------------|
| Method                  | Sol-gel                                           | Solid State Reaction                               |
| Space Group             | I4/mmm                                            | I4/mmm                                            |
| Structure               | Tetragonal                                        | Tetragonal                                        |
| \( a = b \) (Å)         | 3.7822(2)                                         | 3.774                                             |
| \( c \) (Å)             | 13.2213(2)                                        | 13.231                                            |
| \( V(Å^3) \)            | 189.1331                                          | 186.952                                           |
| average crystallite size (nm) | 41.835                                      | -                                                 |
| Discrepancy factor      | GoF                                               | -                                                 |
|                         | \( R_{wp} \) (%)                                  | 10.0451                                           |
|                         | \( R_p \) (%)                                     | 7.7906                                            |

**Figure 2.** SEM micrograph of LSCO.

EDS result shows that the obtained LSCO sample has already consisted with the appropriate elements (Figure 3). However, there is a lack of lanthanum element on the results found. It may be the case because the precursor used in the form of \( \text{La}_2\text{O}_3 \) have not been dissolved perfectly in nitric acid to obtain a nitrate form of lanthanum element. Thus, it is harder for \( \text{La}_2\text{O}_3 \) to react with another precursor to form an LSCO compound. Additionally, EDS result did not detect any element besides its precursor, so it can be said that obtained LSCO sample has a high purity level.

The slight difference between the calculated value and the measured value (Table 2) for the constituent element in the sample can be addressed to the sol-gel which is used to synthesize the sample. In this sol-gel method, all the precursors have to convert into metal nitrate form. Moreover, all the precursors are needed to available in solution form as it is easier for all the precursors to react chemically. During the step to pour the precursor in solution form to the compartment for reaction,
there is a leftover which suspected to contain several elements. Thus, the obtained sample is more difficult to achieve chemical composition close to the stoichiometric calculation, because EDS is semiqualitative measured.

Figure 3. The obtained EDS spectrum shows the appropriate elements in the obtained LSCO sample.

| Element | Calculated (At%) | Measured (At%) |
|---------|-----------------|----------------|
| La      | 26.28           | 23.85          |
| Sr      | 2.29            | 2.26           |
| Cu      | 14.29           | 16.06          |
| O       | 57.14           | 57.83          |
| Total   | 100             | 100            |

4. Conclusion

La$_{1.84}$Sr$_{0.16}$CuO$_4$ compound has been synthesized using the sol-gel method and the crystal structure, morphology, and purity of the sample have been studied. Based on the XRD result, it can be concluded that different synthesis method only affects the lattice parameter of the sample. Furthermore, in order to obtain a single phase sample using the sol-gel method, it is crucial to make sure that all the precursors that were in oxide form have been correctly converted into its metal-nitrate form using the appropriate amount of nitric acid. Moreover, based on the EDS result, it is difficult to obtain a sample with stoichiometric chemical composition using a solution method.

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References

[1] Bednorz J G and Muller Z 1986 Phys B 64 189
[2] Moodenbaugh A R, Xu Y, Suenaga M, Folkerts T J and Shelton R N 1998 Phys Rev B38 4596
[3] Saleem A and Hussain S T 2013 J Surf Interface Mater 1(2) 97
[4] Nguyen N, Studer F and Raveau B 1983 J Phys Chem Solids 44(3) 389
[5] Deganello F, Marci G and Deganello G 2009 J Eur Ceram Soc 29(3) 439
[6] Holzwarth, U and Gibson, N 2011 Nat Nanotechnol 6(9) 534