Structural and morphological characterization of cuprate superconductor La$_{2-x}$Sr$_x$CuO$_4$ ($x=0$ and $x=0.07$) synthesized by sol-gel method

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Abstract. The La$_{2-x}$Sr$_x$CuO$_4$ materials with $x=0$ and $x=0.07$ were prepared by sol-gel method. These materials are the family of cuprate superconductor. These samples were heated three times by drying at 120°C for 2 hours, calcining at 500°C for 5 hours, and sintering at 700°C for 15 hours. The powder sample was pressed and compacted to be a bulk samples. These materials were characterized by X-Ray Diffraction (XRD) to study the structure of materials and Scanning Electron Microscopy – Electron Dispersive Spectroscopy (SEM-EDS) to study morphology and confirm the composition of materials. The results of XRD and High-Score application showed that the structure of both samples is orthorhombic (Cmca/64 space group). The substitution of Sr$^{2+}$ ion with $x = 0.07$ to the La site did not change the crystal structure of material but it showed the variation of lattice parameter and unit cell volume. The variation indicated a decreasing of unit cell volume by substituting Sr$^{2+}$ ion to La site. SEM-EDS characterization showed that both samples have homogeneity and confirmed that Sr$^{2+}$ ion has successfully substituted to La site for La$_{1.93}$Sr$_{0.07}$CuO$_4$ material. It also revealed that composition of both samples is similar to the stoichiometry calculation.

1. Introduction
The family of Cuprate Superconductors based on Lanthanum have studied in recent years. Its special properties have attracted many researchers. The structure, morphology, electrical properties, and superconducting phenomenon are important things of these materials. A superconducting phenomenon was discovered by Onnes in 1911 and he showed the first characteristic of superconductors [1]. Onnes revealed that superconductor materials have zero resistivity at critical temperature ($T_c$). The second characteristic of superconductors was discovered by Meissner and Ochsenfeld. They showed that superconductor refuse the external magnetic field below the critical field. [2].

In 1986, Bednorz and Muller discovered the first high temperature superconductor named Lanthanum Barium Copper Oxide (La$_{2-x}$Ba$_x$CuO$_4$) [3]. Since the discovering, many superconductors based on Lanthanum have been found by researchers such as Lanthanum Srontium Copper Oxide (La$_{2-x}$Sr$_x$CuO$_4$). La$_{2-x}$Sr$_x$CuO$_4$ was called as the high temperature superconductor because it has $T_c$ up to 36K, while the other conventional superconductors have $T_c$ less than 30$^\circ$K [3,4]. La$_{2-x}$Sr$_x$CuO$_4$ is the unconventional superconductor. It has attracted attention of the researchers because of their complicated properties such as their electrical properties and superconducting phenomenon which are different from the conventional superconductor. It is an insulator antiferromagnetic for the parental compound La$_2$CuO$_4$ but it transforms to be a superconductor by adding charge carriers to this material [5,6]. The
charge carries appear in CuO$_2$ plane by substituting Sr$^{2+}$ ion to the La site or inserting the oxygen to material [7]. La$_{2-x}$Sr$_x$CuO$_4$ materials have been synthesized in many methods such as thin film and solid state reaction. The general structure of these materials is Perovskite structure [8]. It consists of two layer; CuO$_2$ planes and blocking layers. Superconducting phenomenon appears in CuO$_2$ planes which are separated by blocking layers such as La, Ba, and Sr.

In this paper, we report on the common characteristics of La$_{2-x}$Sr$_x$CuO$_4$ with x = 0 and x = 0.07 such as the structure and the morphology. We will study the effect of substituting Sr$^{2+}$ on the materials for their phase, lattice parameter, crystallite size, homogeneity, and purity of samples.

2. Material and Method
The La$_{2-x}$Sr$_x$CuO$_4$ materials with x=0 and x=0.07 were prepared by sol-gel method. The precursors of this method were La$_2$O$_3$, Sr(NO$_3$)$_2$.3H$_2$O and Cu(NO$_3$)$_2$. All precursors were calculated by stoichiometry method and then weighed by digital balance. Sr(NO$_3$)$_2$.3H$_2$O and Cu(NO$_3$)$_2$ were dissolved by aqueous solution, while La$_2$O$_3$ was dissolved by nitrate acid and aqueous solution to get Lanthanum Nitrate solution. All precursors were mixed into the beaker glass and added with citric acid as catalyst compound to accelerate the reaction. The solution was evaporated on a hot-plate at 70°C-80°C with continuous stirring. The ammonia was added to the solution to get pH = 7. The sol-gel method changed the solution to the gel form. It was occurred for about 3 hours before the samples were heated three times. The gel samples dried at 120°C in the oven to evaporate samples and changed gel samples to the powder form. The powder sample was heated at 500°C for 5 hours called calcining to evaporate the organic compound like nitrate. It was pressed to get a bulk samples with five tons of pressure and then sintered at 700°C for 15 hours in a furnace to grow the grain of samples.

The bulk samples were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscopy – Electron Dispersive Spectroscopy (SEM-EDS). The structural characterization was obtained by X-Ray Diffraction (XRD). The samples were measured at room temperature with 10° to 90° (2θ) and 0.02° of step size. The result of this measurement was analyzed by High Score Application to get a crystal structure, lattice parameter, unit cell volume, and space group of samples. The surface morphology of the samples was characterized by Scanning Electron Microscopy (SEM). This characterization used 20,000 times magnification to study the surface morphology, grain size, and homogeneity of samples. The samples were also characterized by Electron Dispersive Spectroscopy (EDS) to confirm the composition and purity of samples.

3. Result and Discussion

The structure of La$_2$CuO$_4$ and La$_{1.93}$Sr$_{0.07}$CuO$_4$ has been investigated by X-Ray Diffraction (XRD). Figure 1 above shows the XRD pattern of these samples. According to XRD pattern, both samples have
the same diffraction pattern. It showed that there is no change of crystal structure when Sr$^{2+}$ ion was substituted to the La site. The data from XRD measurement was analyzed by High Score Application to study the phase, crystal structure, lattice parameter, unit cell volume, and crystallite size. The result showed that both samples have an orthorhombic structure with Cmca/64 space group. The absence of the residual peaks from the raw materials indicated that both samples have a single phase. The result is also revealed in previous research [9]. Substitution of ion Sr$^{2+}$ to the La site did not change the crystal structure of samples but it showed the variation of lattice parameter and unit cell volume (shown in Table 1). Figure 2 shows the peak of both samples at the certain angle. There is a shifting peak when the parental compound was substituted by Sr$^{2+}$ ion. The peak of parental compound La$_2$CuO$_4$ has appeared in 31.1949°, while the peak of doped sample La$_{1.93}$Sr$_{0.07}$CuO$_4$ is appeared in 31.0656°. It indicated that the substitution of a divalent ion to the La site can change the lattice parameter, and it affects to the unit cell volume of samples. Figure 2 also shows a difference of the peak’s width between La$_2$CuO$_4$ and La$_{1.93}$Sr$_{0.07}$CuO$_4$. A broadening of peak appeared in doped samples La$_{1.93}$Sr$_{0.07}$CuO$_4$ although the elongation is not specific.

The result of Rietveld refinement using High Score Application is showed in Table 1. It contained of crystal structure, space group, lattice parameter, unit cell volume, Goodness of Fit (GoF), and crystallite size of La$_2$CuO$_4$ and La$_{1.93}$Sr$_{0.07}$CuO$_4$. Table 1 below shows that both samples has the same crystal structure and space group. Substitution of Sr with concentration 0.07 changed the lattice parameter of the sample. The lattice parameter of a and b decreased when Sr$^{2+}$ ion has successfully substituted to the La site, while the lattice parameter of c increased. It is induced by an appearance of strain along the c axis, so there was an expansion of c lattice parameter and a compression of a and b lattice parameter. The expansion of c axis has occurred because the radius of Sr$^{2+}$ ion (1.3 Å) is larger than the radius of La$^{3+}$ ion (1.172 Å). It was revealed by previous research that the c-axis increases when the doping of Sr increases [10]. A decreasing of lattice parameter (a and b) affected to the electrical properties of both samples. In cuprate superconductor, an electrical phenomenon such as superconductivity appeared in the CuO$_2$ plane (parallel with a-axis and b-axis) because there were blocking layers that supplied charge carriers in CuO$_2$ plane due to the substitution of divalent ion in the La site [6]. The distance of each copper atoms and d(Cu-O) in the CuO$_2$ plane decreased when the a and b lattice parameter decreased so the charge carriers could transport along the CuO$_2$ plane easily [11]. It caused the resistivity of samples decreased upon an increase of a Sr$^{2+}$ ion. It is revealed in the previous research that the resistivity of La$_{2.08}$Sr$_3$CuO$_4$ decreased when the doping concentration of Sr$^{2+}$ increased [12]. The crystallite size of La$_{1.93}$Sr$_{0.07}$CuO$_4$ (419.8 Å) was also smaller than the parental compound La$_2$CuO$_4$ (585.2 Å). According to the analysis, it is concluded that the crystal structure, lattice parameter, and unit cell volume are important characteristic because they are related to the physical properties such as the electrical properties. A goodness of Fit (GoF) showed the compatibility between the XRD pattern of samples and XRD pattern from a database. The GoF value of both samples indicated that XRD pattern of samples is compatible with database and both samples have a single phase.

| Crystal Structure | Orthorhombic | Orthorhombic |
|------------------|--------------|--------------|
| Space Group      | Cmca (64)    | Cmca (64)    |
| Lattice Parameter a [Å] | 5.3608      | 5.3493      |
| Lattice Parameter b [Å] | 5.3968      | 5.3651      |
| Lattice Parameter c [Å] | 13.1593     | 13.1974     |
| Unit Cell Volume [Å$^3$] | 380.7159    | 378.7620    |
| Crystallite Size [Å]    | 585.2       | 419.8       |
| GoF               | 1.1         | 1.3         |
| $<$Cu-O$>$ [Å]     | 1.904       | 1.89        |
Figure 3(a) and 3(b) showed the surface morphology of La$_2$CuO$_4$ and La$_{1.93}$Sr$_{0.07}$CuO$_4$. The result of the measurement showed that the surface of both samples have homogeneity. Actually, the grain of both samples was not really clear although the magnification of image up to 20,000 times. It can be seen that the grain size of the doped sample La$_{1.93}$Sr$_{0.07}$CuO$_4$ is similar with the grain size of the parental compound La$_2$CuO$_4$, but the measurement of the grain diagonal showed that the grain size of the doped sample is smaller than the parental compound. It was compatible with the result of the crystallite size of La$_{1.93}$Sr$_{0.07}$CuO$_4$ compared to La$_2$CuO$_4$. The average grain size of La$_{1.93}$Sr$_{0.07}$CuO$_4$ is 156.425 nm, while the average grain size of La$_2$CuO$_4$ is 164.620 nm.

Figure 4 showed the EDS result of La$_2$CuO$_4$ and La$_{1.93}$Sr$_{0.07}$CuO$_4$. These results were used to confirm the composition of both samples and the purity. The peak of Sr was seen in the spectrum of the EDS result for doped sample La$_{1.93}$Sr$_{0.07}$CuO$_4$. It revealed that Sr$^{2+}$ ion has successfully substituted to the La site. The spectrum contained the peaks of all compound, such as La, Cu, and O for La$_2$CuO$_4$ and there was Sr for doped sample La$_{1.93}$Sr$_{0.07}$CuO$_4$. The comparison between the composition of samples according to the EDS result and the stoichiometry calculation was seen in Table 2. The EDS result was similar to the calculation, although there was a little bit of difference between the values of the composition. It was caused by the characteristic of the EDS result is semi-quantitative. The EDS result also revealed that there is no other compound contained in the samples, so it can be concluded that both samples have high purity.
**Tabel 1.** The Composition of La$_2$CuO$_4$ and La$_{1.93}$Sr$_{0.07}$CuO$_4$ samples

|               | La     | Sr     | Cu    | O      | La  | Sr  | Cu   | O     |
|---------------|--------|--------|-------|--------|-----|-----|------|-------|
| La$_2$CuO$_4$ | 26.88  | 0      | 15.57 | 57.55  | 28.57| 0   | 14.29| 57.14 |
| La$_{1.93}$Sr$_{0.07}$CuO$_4$ | 25.72  | 1.16   | 14.06 | 59.06  | 27.57| 1   | 14.29| 57.14 |

4. Conclusion
La$_2$CuO$_4$ and La$_{1.93}$Sr$_{0.07}$CuO$_4$ materials have successfully synthesized by sol-gel method. The result of XRD showed that both samples has an orthorhombic structure with Cmca/64 space group. The substitution of Sr$^{2+}$ ion to the La site did not change the crystal structure but it decreased the lattice parameter (a and b), unit cell volume, and crystallite size of sample, so it affected to the distance of each copper atoms in CuO$_2$ plane and the distance between Cu and O (d<Cu-O>). The result of SEM indicated a decreasing of grain size for doped sample La$_{1.93}$Sr$_{0.07}$CuO$_4$ compared to the grain size of parental compound La$_2$CuO$_4$. It also showed that both samples has homogeneity. The composition and the purity of samples were known by EDS. It showed that the composition of the sample is similar with the stoichiometry calculation, so it concluded that both samples have high purity.

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