The effect of heating treatment in electron doped superconductor Eu$_{1.85}$Ce$_{0.15}$CuO$_{4+\alpha-\delta}$

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Abstract. Electron-doped superconductor Eu$_{1.85}$Ce$_{0.15}$CuO$_{4+\alpha-\delta}$ has been synthesized using solid state reaction method. The purpose of this research is to study the effect of heating process with and without annealing treatment to its superconductivity. The sample without annealing treatment was covered by CuO to prevent the excess of oxygen in sample during heating process. All samples were characterized by XRD, resistivity and susceptibility measurement to study structure, electrical and magnetic properties of Eu$_{1.85}$Ce$_{0.15}$CuO$_{4+\alpha-\delta}$ samples with different heating process. From XRD measurement, it is found that all samples have tetragonal crystal with T' structure. From magnetic susceptibility and resistivity measurement, superconductivity was observed only in the sample with annealing treatment. The absence of superconductivity in sample without annealing was probably due to the existence of excess oxygen.

1. Introduction

Superconductivity is a phenomenon when the resistivity became zero at low temperature below its critical temperature called $T_c$. This $T_c$ depends on the structure and composition of the material. First discovery of High-$T_c$ Superconducting Cuprates (HTSC) is cuprates compound called 214 cuprates system. There are two types of 214 cuprates systems, hole-doped and electron-doped superconductor. For hole-doped system, some researchers were performed and reported various properties such as impurity effects, ground state, thermal conductivity and magnetic properties [1-7]. For electron-doped, in other side, only a few reports were published [8-11]. One of possible reason is some difficulties in preparing high quality samples.

The formula of 214 electron-doped cuprates is Ln$_{2-x}$Ce$_x$CuO$_4$ ($Ln$ = La, Pr, Nd, Sm, Eu). Compared with other compound of electron-doped cuprates, Eu$_{2-x}$Ce$_x$CuO$_4$ (ECCO) has the narrowest range of doping concentration. However, the study of ECCO is very important because nonmagnetic properties of Eu give some advantages to explore magnetic properties in CuO$_2$ plane without any disturbing from rare earth magnetic moment [8, 9].

In process of synthesis, ECCO formed as-grown sample after sintering process. Usually, in as-grown sample, the superconducting phase has not formed yet even though the value of doping concentration was in optimum-doped condition. The oxygen content became one of important
parameters to form superconducting phase [9]. Controlling oxygen content can be done in several ways, such as, by flowing argon gas (Ar) with a certain time and temperature, called annealing process. In addition to the treatment of annealing, oxygen content can also be controlled by covering the sample with CuO material during the second sintering process. Covering by CuO is expected to prevent the addition of oxygen content during the heating process.

In this research, we synthesized electron-doped superconductor ECCO to study the effect of heating process with and without annealing treatment to its superconductivity.

2. Experiments
The samples of ECCO were prepared by the solid-state reaction method with $x = 0.15$. The raw materials of $\text{Eu}_2\text{O}_3$, CeO$_2$, and CuO were grinded finely. After that, the samples were pre-fired in the furnace at 900°C for 20 hours. After pre-fired, samples were grinded again finely and were sintered at 1050°C for 16 hours. The heating treatment was performed in different ways for each sample. Some samples were covered by CuO in order to prevent the addition of oxygen content during sintering, and other samples were annealed in argon gas (Ar) flow at 900°C for 10 hours. The samples were characterized by X-ray diffraction (XRD), resistivity by four point probe method and magnetic susceptibility by superconducting quantum interference device (SQUID) measurement.

3. Result and Discussion
The first grinding process of ECCO was visually produced a grey sample, indicating that the mixture of the materials has been homogeneous as shown in figure 1(a). After pre-fired process, the colour of samples changed to be black as shown in figure 1(b). The first sintering process was produced a fairly hard and black sample, shown in figure 1(c). The sample is formed into a 10 mm of pellet by using a hydraulic press as shown in figure 1(d).

![Figure 1](image1.png)

After the sample was formed into a pellet, one of the samples was subjected to annealing treatment at 900°C for 10 hours as shown in figure 2(a) and other samples were subjected to cover by CuO material as shown in figure 2(b).

![Figure 2](image2.png)
XRD pattern of sample Eu$_{1.85}$Ce$_{0.15}$CuO$_{4+\alpha-\delta}$ are shown in figure 3. Figure 3(a) shows samples with annealing treatment ($\delta = 0.04$), and figure 3(b) sample covered by CuO without annealing treatment.

![Graph](image)

**Figure 3.** XRD pattern for ECCO samples: (a) with annealing treatment and (b) covered by CuO without annealing treatment.

All samples have shown tetragonal crystal with T' structure of common electron-doped system. The analysis results show the values of lattice parameters ($a$, $c$) and unit cell volumes ($V$) as shown in table 1.

| Sample                  | $a$ ($\text{Å}$) | $c$ ($\text{Å}$) | $V$ ($\text{Å}^3$) |
|-------------------------|------------------|-----------------|-------------------|
| Covered by CuO          | 3.90868          | 11.84645        | 180.9877          |
| Annealing treatment     | 3.90914          | 11.85363        | 181.1395          |

The values of lattice parameters $a$ and $c$ for samples without annealing had smaller than that of the samples with annealing treatment.

![Graph](image)

**Figure 4.** Graph $\chi$-T for ECCO samples (a) with annealing treatment and (b) covered by CuO without annealing treatment.
Figure 4 shows magnetic susceptibility measurements from 2 K to 20 K for samples $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4+\alpha-\delta}$ with $\delta = 0.04$ (figure 4(a)) and samples covered by CuO without annealing treatment (figure 4(b)). The result of magnetic susceptibility measurement for $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4+\alpha-\delta}$ with $\delta = 0.04$ [9] shown $T_c$ at around 12 K. However, for samples covered by CuO, superconductivity did not appear down to 2 K.

Figure 5 shows resistivity measurements for ECCO sample with annealing treatment with $\delta = 0.04$ (figure 5(a)) [9], and sample with $\delta = 0$ or covered by CuO (figure 5(b)).

![Graph ρ-T for ECCO samples](image)

**Figure 5.** Graph ρ-T for ECCO samples (a) with annealing treatment and (b) covered by CuO without annealing treatment.

For samples with annealing treatment, the trace of superconductivity observed at 12 K. For samples covering by CuO, resistivity increases with decreasing temperature without any trace of superconductivity. This result indicated that the value of oxygen content still cannot be controlled by covering the samples during sintering process.

4. Conclusions

Electron doped superconductor of ECCO has been synthesized with different heating treatment, namely, with and without annealing process. From XRD measurements, it is found that all samples have tetragonal crystal with T’ structure. From susceptibility and resistivity measurement, it is found that superconductivity was observed in sample with annealing process with $T_c$ around 12 K. However, no trace of superconductivity was observed in samples without annealing process, which is probably due to the excess of oxygen still exist even though samples were covered by CuO during sintering process.

Acknowledgment

We would like to thank Professor Yoji Koike and Koike Laboratory members for assisting in measuring of XRD characterization, resistivity and susceptibility measurement at Department of Applied Physics Graduate School of Engineering at Tohoku University. These works were supported by Academic Leadership Grant Universitas Padjadjaran 2017, No: 872/UN6.3.1/LT/2017 and International Research Collaboration and International Publication Grant No. 718/UN6.3.1/PL/2017.

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