Study of structure and resistivity of electron-doped superconducting cuprates \( \text{Eu}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-y}\text{Zn}_y\text{O}_{4+\alpha-\delta} \)

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Abstract. Partially Zn-substituted for Cu in electron-doped superconducting cuprates of \( \text{Eu}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-y}\text{Zn}_y\text{O}_{4+\alpha-\delta} \) (ECCZO) with \( y = 0, 0.01, 0.02, 0.05 \) and various \( \delta \) values have been studied in order to elucidate the effect of nonmagnetic impurity of Zn to their structure and resistivity properties in the electron-doped cuprates. It has been found that the main peaks of T’ structures are clearly observed in all samples. Superconductivity disappeared with Zn substitution for Cu in electron-doped system of ECCZO.

1. Introduction
Mechanism of high \( T_c \) superconducting cuprates (HTSC) has been one of interesting topic to be studied in order to develop these materials for several applications. Based on charge carrier, there are two system of HTSC, namely, hole-doped system and electron-doped system. When conducting planes in HTSC lose one electron, one mobile hole remains in the planes, leading to the formation of a hole-doped system of HTSC. On the other hand, when conducting planes get an excess electron, the system forms an electron-doped HTSC. For hole-doped system especially La-based 214 cuprates, some reports were published to explore various properties such as magnetic properties, impurity effect, electronic phase diagram and conductivity [1-8]. Different with hole-doped system, only limited reports were published for electron-doped system [9-12] so that some properties in electron-doped system are still needed to be explored to understand mechanism of HTSC in electron-doped system.

For the crystal structure, both systems have common structures consist of both the conduction layer and the charge reservoir layer. The structure of 214 cuprates is basically tetragonal as shown in Figure 1. Each cooper ion is strongly bonded to four oxygen. There are different configurations of conducting layer between hole-doped and electron-doped system. In hole-doped system of \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \), cooper ion and oxygen form octahedral configuration. The structure is called the T structure. Oxygen atoms are located above and below each Cu atom, called apical oxygen as shown in Figure 1(a). In electron-doped system of \( \text{Ln}_{2.5}\text{Ce}_0\text{CuO}_4 \) with Ln is rare earth elements of Nd, Pr, Sm or Eu, cooper ion and oxygen form planar configuration. The structure is called the T’ structure as shown in Figure 1(b). Superconductivity in electron-doped system is obtained after removing the oxygen excess at apical site that exist in the sample during heating or sintering process. This is one of the reason for difficulty in preparing high quality electron-doped superconductivity.
The study of relationship between some physical properties and superconductivity in hole-doped and electron-doped system via the impurity effect has also been intensively studied [5,7,10,13]. It is found that the superconducting volume fraction in hole-doped system of La\text{$_2$-$x$}Sr\text{$_x$}CuO\text{$_4$} is more significantly decreased by a small amount of nonmagnetic impurity of Zn for Cu than that by magnetic impurity of Ni [8]. In electron-doped system, the superconductivity is suppressed through the magnetic impurity of Ni for Cu more markedly than through the Zn substitution [14].

The study of structure and crystallite size associated with the effect of nonmagnetic impurity of Zn for Cu in electron-doped system is also very limited. Here, we reported the study of structure and transport properties in electron-doped system of Eu\text{$_{2-x}$}Ce\text{$_x$}CuO\text{$_4$} in order to elucidate the effect of nonmagnetic impurity of Zn to their structure and resistivity properties in the electron-doped cuprates.

![Figure 1](image1.png)  
*Figure 1.* Crystal structure of hole-doped superconducting cuprates of La\text{$_2$-$x$}Sr\text{$_x$}CuO\text{$_4$} (a), and electron-doped cuprates of Nd\text{$_{3-x}$}Ce\text{$_x$}CuO\text{$_4$} (b).

2. Experimental

Electron-doped cuprates of Eu\text{$_{1.85}$}Ce\text{$_{0.15}$}Cu\text{$_{1.85}$}Zn\text{$_y$}O\text{$_{4+y-\delta}$} with \( y = 0 \) - 0.05 were prepared by the ordinary solid-state reaction method. As-grown samples were obtained after sintering process at 1050°C for 16 h. The oxygen excess (\( \alpha \)) during sintering process was removed by flowing Ar gas at various temperatures in a range of 900°C – 950°C for 10 h – 15 h. Values of removed oxygen by annealing (\( \delta \)) were estimated from the weight change before and after annealing. All of the samples were characterized by the powder x-ray diffraction (XRD) measurements and electrical resistivity measurements at Graduate School of Engineering, Tohoku University, Japan.

3. Results and Discussion

XRD pattern of electron-doped system of Eu\text{$_{1.85}$}Ce\text{$_{0.15}$}Cu\text{$_{1.85}$}Zn\text{$_y$}O\text{$_{4+y-\delta}$} (ECCZO) with \( y = 0, \delta = 0 \) (a) and \( y = 0, 0.01, 0.02, 0.05 \) in various \( \delta \) values of 0.041 (b), 0.090 (c), 0.107 (d), 0.045 (e), respectively, were shown in Figure 2. For reference, the theoretical positions of XRD pattern of Eu\text{$_{1.85}$}Ce\text{$_{0.15}$}CuO\text{$_4$} with selected main peaks from ICSD (code: 72249) [15] were also displayed (f). Main peaks of T’ structures were clearly observed in all samples.
Figure 2. XRD pattern of Eu$_{1.85}$Ce$_{0.15}$Cu$_{1-x}$Zn$_x$O$_{4+\delta}$ with $y=0$, $\delta=0$ (a) and $y=0$ (b), 0.01 (c), 0.02 (d), 0.05 (e) in various $\delta$ values. For reference, XRD pattern of Eu$_{1.85}$Ce$_{0.15}$CuO$_4$ data with ICSD code 72249 [15] (f) are also displayed.

Figure 3 shows the typical lattice parameters in the $a$-axis, $c$-axis and volume of crystal as function of Zn concentration of $y$. The value of $a$-axis stay almost unchanged as the $y$ value varies. One of the reason is the absence of apical Cu-O bonds makes no Jahn-Teller effect in ECCZO samples. Jahn-Teller distortion in the hole-doped system which has apical oxygen ions makes the apical Cu-O bonds longer than the Cu-O bonds in the CuO$_2$ plane, while substitution of Zn for Cu has tendency to equalize the bond lengths between the apical Cu-O bonds and the Cu-O bond in the CuO$_2$ plane. The value of $c$-axis and volume of crystal slightly increased with very small changed as increasing $y$ which is probably due to the slightly different size between Zn and Cu.
Figure 3. Lattice parameters in the $a$- and $c$-axis as function of Zn concentration of $y$ in $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-y}\text{Zn}_{y}\text{O}_{4+\alpha-\delta}$.  

Figure 4 shows temperature dependence of resistivity of $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-y}\text{Zn}_{y}\text{O}_{4+\alpha-\delta}$ with $y = 0.01$, $0.02$, $0.05$ with various $\delta$ values. For $y = 0$, the trace of superconductivity in temperature dependence of resistivity was reported [16]. For $y = 0.01$, $0.02$, and $0.05$, resistivity increased with decreasing temperature. It is found that Zn substitution for Cu was affected in destruction of superconductivity in electron-doped system of ECCZO which is due to the effect of Zn in localized charge carriers in electron-doped system.

Figure 4. Temperature dependence of resistivity of $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-y}\text{Zn}_{y}\text{O}_{4+\alpha-\delta}$ with $y = 0.01$, $0.02$, $0.05$ with various $\delta$ values.

4. Summary
Polycrystalline samples of electron-doped system of $\text{Eu}_{1.85}\text{Ce}_{0.15}\text{Cu}_{1-y}\text{Zn}_{y}\text{O}_{4}$ with $y = 0$, $0.01$, $0.02$, $0.05$ and various $\delta$ values have studied in order to study effect of Zn impurity for Cu to its structure and resistivities. From XRD pattern, it is found that all the main peaks of T’ structures are observed.
From resistivity measurements, it is found that Zn substitution for Cu was affected in destruction of superconductivity in electron-doped system of ECCZO, which is due to the effect of Zn in localized charge carriers in electron-doped system.

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