



Article **Changes in the Structural Parameters and Effective Magnetic Moment of Eu**_{2-x}Ce_xCuO_{4+ $\alpha-\delta$} by Zn Substitution

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Abstract: The effect of nonmagnetic Zn impurities on the structural parameters and effective magnetic moment of electron-doped superconducting cuprates $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$ (ECCZO) with x = 0.10 and 0.15 and y = 0 and 0.01 has been investigated using XRD and SQUID measurements. From XRD measurements, it is found that the lattice parameter of *c* and the Cu-O bond length increase with increasing y. The crystallite size of ECCZO samples was relatively smaller than the sample without impurities determined by the Debye-Scherrer equation and the W-H Plot method. Changes in the lattice parameters of c and Cu-O bond length can affect the appearance of superconductivity (T_c) . The smaller the value of the lattice parameter of *c* and the Cu-O bond length causes the distance between the conducting layer and the charge reservoir to be close enough so that the charge transfer process becomes easier. From the magnetic susceptibility measurement, paramagnetic characteristics were observed for samples with x = 0.10. Meanwhile, for samples with x = 0.15, diamagnetic characteristics can be identified in sample with y = 0. The onset of T_c was observed around 11 K, as indicated by a change from paramagnetic to diamagnetic characteristics. The superconductivity phase disappears with y = 0.01. The effective magnetic moments in samples with y = 0 are smaller than those in samples with y = 0.01. The effective magnetic moment in ECCZO can be contributed by Cu²⁺. When the amount of Cu²⁺ decreases due to the addition of nonmagnetic Zn²⁺ atoms, the overall effective magnetic moment value also decreases. Another possibility that causes a decrease in the value of the magnetic moment of the ECCZO is the existence of stripe-pinning model, which results in suppressed superconductivity by Zn.

Keywords: ECCZO; effective magnetic moment; electron-doped; structural parameters; Zn impurities

1. Introduction

High critical temperature superconducting cuprates (HTSC) have been researched and studied in recent decades. These HTSC materials have a variety of interesting properties and behaviors that need to be studied and solved. HTSC has a parent compound, which is an antiferromagnetic-ordered Mott insulator. The parent compound of HTSC will become a superconductor if the charge carriers, both hole, and electron are doped [1–6]. One example of a parent compound of HTSC is R_2CuO_4 (R = La, Eu, Nd, Pr, or Sm). For a



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). hole-doped system, superconductor is formed when a part of La³⁺ is doped by Sr²⁺ to form the superconductor La_{2-x}Sr_xCuO₄ with maximum $T_c \sim 36$ K [1,2]. As for the electron-doped system, the superconductor is formed when a part of Eu, Nd, Pr, or Sm is doped by Ce⁴⁺ to form a superconductor (Eu,Nd,Pr,Sm)_{2-x}Ce_xCuO₄ with maximum $T_c \sim 24$ K [3,4]. Many studies such as structure, electrical, and magnetic properties, both in experiments, and theories have been carried out in hole-doped systems [7–21]. However, research on electrondoped systems is still limited [22–27]. This is because the structure, electrical properties, and magnetic properties of electron-doped HTSC are highly dependent on oxygen content which is very difficult to control [22–27]. One way to solve this problem is to classify the samples based on oxygen content, namely small and large reduced oxygen content [24]. With this classification, the study of structure, electrical and magnetic properties can be carried out more suitable. These properties are essential to be studied to elucidate the origin of the appearance of superconductivity in the HTSC.

One of the studies that has also attracted the attention of researchers to investigate the mechanism of superconductors is the study of the effect of nonmagnetic impurities. In the hole-doped system, the effect of nonmagnetic impurities can confirm the stripe pinning model. Tranquada et al. first reported a stripe-pinning model with a study of neutron scattering in a hole-doped system to investigate a mechanism called the 1/8 anomaly, which is the region where a sharp decrease in the value of $T_{\rm c}$ at the hole concentration p = 1/8 was observed [12]. This phenomenon is interesting to be studied whether this model also exists in the electron-doped system or not. In previous studies, the addition of Zn to the Pr_{1-x}LaCe_xCuO₄ electron-doped system did not provide clear information about the existence of the stripe pinning model due to the dominance of the magnetic moment of Pr [24]. Therefore, it is necessary to study electron-doped using another system, namely $Eu_{2-x}Ce_xCuO_4$ (ECCO). This system was chosen because Eu does not have a magnetic moment in the ground states [27]. By using $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_4$ (ECCZO), it is expected that the effect of Zn impurities on the stripe pinning model can be well observed. To find out whether the effect of Zn impurity in this ECCZO material can provide information about the stripe pinning model, it is necessary to study the effect of the Zn impurity on the structure and magnetic properties as the first step. Studies on the electrical and magnetic properties of electron-doped $Eu_{1.85}Ce_{0.15}Cu_{1-y}Zn_yO_4$ with x = 0.15have been carried out. For y = 0, the T_c of sample was 13 K [25]. With the addition of Zn only 1% (y = 0.01), T_c completely disappeared, indicating that 1% of Zn impurity can disturbed the superconductivity [25]. Furthermore, 1% of Zn impurity can also reduce the radius of electron localization (r) in the normal state at low temperatures, which may be related to the proof of stripe-pinning effects by Zn in the electron-doped system of ECCZO [25,26]. However, a detailed discussion of the changes in the structural parameters and effective magnetic moment has not been reported. Changes in the structural parameters and magnetic moments can be used as a performance indicator of Zn substitution for Cu in electron-doped superconducting cuprates.

Here, we report the effect of Zn impurity with y = 0.01 on the structure and magnetic properties in ECCO with x = 0.10 and 0.15 to obtain information of detail changes in the structural parameters and effective magnetic moment of ECCZO. We have chosen x = 0.10 because around this concentration, the 1/8 anomaly can also be clearly observed in the hole-doped system. Meanwhile, we have chosen x = 0.15 with the consideration that this concentration has the highest T_c among other concentrations of ECCO material. The structural parameters were analyzed from XRD data using Rietveld refinement analysis, and the crystallite size of samples was calculated using the Debye–Scherrer equation and Williamson–Hall Plot method (W-H Plot). Meanwhile, the effective magnetic moment is obtained from analyzing the susceptibility data.

2. Materials and Methods

Polycrystalline samples of $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$ with x = 0.10; 0.15 and y = 0; 0.01 were synthesized by the solid-state reaction method. The raw materials of Eu_2O_3 , CuO,

CeO₂, and ZnO were prepared to get 2.5 g in a total of ECCZO. All raw materials were ground for one hour to form high homogeneous precursors. The homogeneous powders of precursors were pre-fired in the air at 900 °C for 20 h. After pre-fired, all samples were re-ground, compressed into a pellet, and sintered at 1000 °C for 20 h, then annealed at 910 °C for 10 h in Ar gas flow to reduce the excess oxygen content (α) [22–27]. The reduced oxygen content (δ) was calculated from the different weights of each sample before and after annealing treatment. The values of δ for ECCZO samples are 0.047 for x = 0.10 and y = 0; 0.041 for x = 0.15 and y = 0; 0.037 for x = 0.10 and y = 0.01; and 0.090 for x = 0.15 and y = 0.01.

The crystal structure was characterized by X-Ray Diffraction (XRD) (Bruker AXSGmbH-Karlsruhe, Germany) with Cu- K_{α} radiation in the range of $2\theta = 10-70^{\circ}$, the existence of the Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+ $\alpha-\delta}$} phase was analyzed by using Bruker-Topas software (version 6) with Rietveld refinement analysis [28,29]. Identification of the diffraction peaks of experimental result matched with the reference of ICSD No. 98-007-2249 with formula Eu_{1.85}Ce_{0.15}CuO₄ [30]. The Rietveld refinement analysis is used for obtaining the crystal structure, lattice parameter, and bond length of samples. The Debye–Scherrer equation and W-H Plot method were used to determine the crystallite size of ECCZO samples. The measurements of magnetic susceptibility (χ) were performed using a Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design MPMS XL, San Diego, CA, USA) in temperatures between 2 K and 30 K with 5 Oe of magnetic field on field-cooling [25,26].

3. Results and Discussion

3.1. X-ray Diffraction Analysis

Figure 1 shows the XRD patterns of $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$ with x = 0.10; 0.15 and y = 0; 0.01. The major peaks of all samples are well fitted with the reference of ICSD No. 98-007-2249 [30]. Analyzes of the structural parameters from XRD data confirmed that all samples have a T' and tetragonal crystal structure ($a = b \neq c$), which is represented by the main peaks at Miller indexes of (013) and (110) and included to the space group of I4/mmm. The small amount of impurity peak was detected at $2\theta = 34^{\circ}$ as the CeO₂. However, the small amount of impurities did not affect the quality of the samples as indicated by the purity level which had a value greater than 98%. All peaks have the Goodness of Fit (GoF) values of around 1.1–1.4, indicating that the data and fitting model have good agreement.



Figure 1. The XRD pattern of $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$ with x = 0.10 (**a**) and 0.15 (**b**).

Figure 2 shows the crystal structure of $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$ with a tetragonal T' structure consisting of conducting layer of CuO₂ and charge reservoir of (Eu,Ce)-O(1) and

(Eu,Ce)-O(2). The Cu-O(2) bond is in conducting layer, while Eu-O(1) and Eu-O(2) bond are located in the charge reservoir.



Figure 2. Crystal structure of $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$.

The crystallite size (*D*) of samples can be estimated using the Debye–Scherrer formula and W-H plot method. The Debye–Scherrer formula is shown in Equation (1), and W-H plot method is shown in Equation (2) [31,32].

$$D = \frac{K\lambda}{\beta_{hkl} \cos \theta} \tag{1}$$

$$\beta_{hkl}\cos\theta = \varepsilon(4\sin\theta) + \frac{K\lambda}{D}$$
(2)

 β_{hkl} is the FWHM of the diffraction peak, λ is the wavelength of the XRD source, *K* is a shape factor equal to 0.9, θ is the diffraction angle, and ε is the lattice strain [31,32].

Figure 3 shows W-H plot parameter of $\beta_{hkl} \cos \theta$ versus $4 \sin \theta$. The ε value is obtained from the slope on each graph and found to be a positive value indicating the possibility of tensile strain in the samples [33,34]. Furthermore, the crystallite size (*D*) was calculated using the intercept of Equation (2). The values of ε and *D* for each sample are shown in Table 1.

Table 1 shows structural parameters of $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$ with x = 0.10; 0.15 and y = 0; 0.01 obtained from the Rietveld refinement, the Debye–Scherrer equation, and W-H plot of XRD data. It is found that the lattice parameters of *a* are in the range from 3.9056(1) Å to 3.9070(1) Å, while the lattice parameters of *c* are in the range from 11.8369(3) Å to 11.8914(3) Å, and unit cell volume is in the range from 180.693(8) Å to 181.176(7) Å. For x = 0.15 and y = 0, the lattice parameter values obtained in this study are in the similar range as previously reported [22]. The Cu-O bond length was 1.95166(4) Å to 1.95354(5) Å, (Eu,Ce)-O(1) bond length was 2.29032(5) Å to 2.29167(7) Å, (Eu,Ce)-O(2) bond length was 2.63190(5) Å to 2.63597(5) Å.

For samples with y = 0, the lattice parameter of *a* stays almost unchanged with increasing *x*. On the other hand, the lattice parameters of *c* and Cu-O bond length decreased with increasing *x* from 0.10 to 0.15. Changes in lattice parameters of *c* and Cu-O bond length can affect the appearance of superconductivity (T_c). The smaller the value of these parameters causes the distance between the conducting layer and the charge reservoir to be close enough, so that the charge transfer process becomes easier and requires only a minimal energy. This may cause superconductivity (T_c) to occur more easily. Therefore,



the sample with x = 0.15, superconductivity appears with a T_c value of 11 K, while in the sample with x = 0.10, superconductivity is not observed.

Figure 3. W-H Plot of $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$ with x = 0.10 (**a**) and 0.15 (**b**).

Table 1. Structural parameters of $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$ with x = 0.10; 0.15 and y = 0; 0.01.

Samples	<i>x</i> = 0.10		<i>x</i> = 0.15	
$Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$	<i>y</i> = 0	<i>y</i> = 0.01	<i>y</i> = 0	<i>y</i> = 0.01
Space group	I4/mmm	I4/mmm	I4/mmm	I4/mmm
Structure	Tetragonal	Tetragonal	Tetragonal	Tetragonal
Lattice Parameters	Ŭ	0	0	0
a (Å) = b (Å)	3.9056 (1)	3.9058 (1)	3.9070(1)	3.9033 (1)
c (Å)	11.8656 (5)	11.8721 (6)	11.8369 (3)	11.8914 (3)
Volume (Å ³)	180.996 (10)	181.118 (11)	180.693 (8)	181.176 (7)
Bond Length				
$Cu - O(\mathring{A})$	1.95281 (6)	1.95293 (8)	1.95166 (4)	1.95354 (5)
(Eu, Ce) - O(1) (Å)	2.29122 (6)	2.29167 (7)	2.29032 (5)	2.29161 (4)
(Eu, Ce) - O(2) (Å)	2.63424 (7)	2.63498 (9)	2.63190 (5)	2.63597 (5)
Crystallite Size				
Debye–Scherrer (D (nm))	88.61 (1)	84.02 (3)	104.66 (2)	80.66 (5)
W-H Plot (D (nm))	94.83 (5)	97.12 (25)	118.5 6 (5)	104.43 (1)
Strain (ε)	0.642×10^{-4}	0.139×10^{-4}	0.970×10^{-4}	0.245×10^{-4}
Reliability Factors				
Goodness of Fit (GoF)	1.1	1.2	1.4	1.1

However, for the effect of Zn substitution on the structural parameters, the value of lattice parameter of *a* is almost the same with changing *y* value from 0 to 0.01. Meanwhile, the value of lattice parameter of *c* and the Cu-O bond length tiny increased with increasing the value of *y*, which is probably due to the values of ionic radii of Zn^{2+} ($r_{Zn^{2+}} = 0.74$ Å) being greater than ionic radii of Cu^{2+} ($r_{Cu^{2+}} = 0.73$ Å) [35]. The increase of ionic radii when Zn partially substituting the Cu, caused the expansion of the tetragonal unit cell in the vertical direction. As a result, the distance between the charge reservoir and the conduction layer (CuO₂) increases. Comparing the crystallite size value calculated by the Debye–Scherrer equation and W-H plot, it is found that the crystallite size calculated by the Debye–Scherrer equation have a smaller size than those estimated by W-H plot. It is because W-H plot includes the micro-strain effect in the calculation from lattice imperfection. This

result indicated lattice imperfection such as atom dislocation and defects might occur in samples.

The crystallite size of ECCZO samples with y = 0.01 was relatively smaller than the sample with y = 0. This is related to the concentration of impurities. Impurities cause a decrease in the crystal lattice of the ECCZO samples. The increase in the lattice parameter of *c* and the Cu-O bond length and the decrease in crystal size cause the expand of lattice volume and the distance between layers, affecting the decrease in T_c .

3.2. Susceptibility Analysis

Temperature dependences of χ in field cooled in H = 5 Oe for Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+ $\alpha-\delta$} with x = 0.10; 0.15 and y = 0; 0.01 are shown in Figure 4. For x = 0.10, all samples have paramagnetic characteristics with no sign of a superconducting phase. It might be due to several reasons. Firstly, the doping amount is insufficient to change the system from the nonsuperconducting phase to the superconducting phase. As is well known in the phase diagram for electron-doped superconducting cuprates, the superconducting phase is formed in a narrow region with a wide antiferromagnetic region. This is because the dilution effect on the electron-doped superconducting cuprates requires the right amount of doping so that the effect can disrupt the system and the antiferromagnetic phase turns into a superconducting phase. The second possibility is that the excess oxygen content (α) in the samples is not fully reduced. Meanwhile, for samples with x = 0.15, diamagnetic characteristics can be identified in sample with y = 0. The onset of T_c was observed around 11 K, as indicated by a change in paramagnetic to diamagnetic characteristics. It can be seen that the superconductivity phase disappears in sample with y = 0.01.



Figure 4. The magnetic susceptibility (χ) in field cooled in H = 5 Oe versus temperature for $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$ with x = 0.10 (**a**) and 0.15 (**b**).

In the normal state, the value of Curie constant (*C*) can be analyzed by the Curie law described in Equation (3), using χ data in the temperatures ranging from 15 to 30 K [26].

χ

п

$$=\frac{C}{T}$$
(3)

The magnetic moment per unit cell $(n\mu^2)$ and effective magnetic moment (μ_{eff}) can be calculated by Equations (4) and (5) [36].

$$\mu^2 = \frac{3k_BC}{\mu_0} \tag{4}$$

$$\mu_{eff} = \sqrt{3Ck_B / N_A \mu_B^2} = 2.828 \sqrt{C} \ \mu_B \tag{5}$$

 μ , k_B , n, N_A , μ_{eff} , and μ_B are the magnetic moment per atom, Boltzmann's constant, the number of atoms per unit cell, Avogadro's constant, the effective magnetic moment, and the Bohr magneton unit, respectively.

Figure 5 shows the graph of $1/\chi$ for Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+ $\alpha-\delta$} with x = 0.10; 0.15 and y = 0; 0.01. The *C* value, the magnetic moment per unit cell, and the effective magnetic moment can be obtained by extracting of gradient value from each graph in Figure 5.



Figure 5. The graph of $1/\chi$ versus T for $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$ with x = 0.10 (a) and 0.15 (b).

Table 2 shows the value of *C*, $n\mu^2$ and μ_{eff} of Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+ $\alpha-\delta$} with *x* = 0.10; 0.15 and y = 0; 0.01 for temperatures in the range of a normal state from 15 to 30 K. For y = 0, the values of *C*, $n\mu^2$, and μ_{eff} for sample with x = 0.10 were larger than those of x = 0.15. It is probably due to the ordering effect of the parent compound samples, which behave antiferromagnetic, as shown in the phase diagram [27]. Meanwhile, for x = 0.10 and 0.15, the values of C, $n\mu^2$ and μ_{eff} decreased with increasing y. It is known that the effective magnetic moment in this sample can be contributed by Cu^{2+} . This assumption is based on the value of the effective magnetic moment in the ECCO sample, which has a value close to the effective magnetic moment value of the Cu site of 0.60 μ_B/fu on La₂CuO₄ material [37]. When 0.01 of Zn has partially replaced Cu, the effective magnetic moment value of both x concentrations decreased. When the amount of Cu^{2+} decreases due to the addition of nonmagnetic Zn^{2+} atoms, the overall effective magnetic moment value also decreases. Another possibility that causes a decrease in the value of the magnetic moment of the ECCO material when 0.01 of Zn was added is the existence of the dynamical strip correlation of spin and charge that is pinned and stabilized by Zn, which results in suppressed superconductivity. These results are in agreement with those reported on $Eu_{1.85}Ce_{0.15}Cu_{1-\gamma}Ni_{\gamma}O_{4+\alpha-\delta}$ [38] and LSCZO hole-doped superconducting cuprates [7]. The change in the value of the effective magnetic moment of ECCO by Zn is expected to be used as the first indication of the existence of a stripe-pinning model in electron-doped superconducting cuprates.

Table 2. Magnetic parameters values of $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$ with x = 0.10; 0.15 and y = 0; 0.01.

x	у	$C (10^{-2} \text{ emu} \cdot \text{K} \cdot \text{Oe/mol})$	$n\mu^2$ (10^{-18} emu·J·Oe/mol)	$\mu_{eff}\left(\mu_{eta}/fu ight)$
0.10	0 0.01	$\begin{array}{c} 7.50 \pm 0.06 \\ 4.34 \pm 0.01 \end{array}$	$\begin{array}{c} 2.46 \pm 0.02 \\ 1.43 \pm 0.02 \end{array}$	$\begin{array}{c} 0.77 \pm 0.01 \\ 0.59 \pm 0.01 \end{array}$
0.15	0 0.01	$\begin{array}{c} 7.34 \pm 0.02 \\ 5.66 \pm 0.05 \end{array}$	$\begin{array}{c} 2.41 \pm 0.01 \\ 1.86 \pm 0.02 \end{array}$	$\begin{array}{c} 0.76 \pm 0.02 \\ 0.67 \pm 0.06 \end{array}$

4. Conclusions

Electron-doped superconducting cuprates of $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$ with x = 0.10; 0.15 and y = 0; 0.01 were successfully synthesized to investigate the effect of partial substitution Zn for Cu on the changes of structural parameters and effective magnetic moment. From XRD measurements, it is found that all samples have T' tetragonal structure. For samples with y = 0, the lattice parameter of *a* stays almost unchanged with increasing *x*. On the other hand, the lattice parameters of *c* and Cu-O bond length decreased with increasing x. The crystallite size of ECCZO samples with y = 0.01 obtained using the Debye–Scherrer equation and W-H Plot was relatively smaller than the sample with y = 0. Lattice parameters of c, Cu-O bond length, and crystal size of the sample with x = 0.15 are smaller than those of x = 0.10. The shrinking of these parameters may affect the appearance of superconductivity $(T_{\rm c})$. When these parameters decrease, the distance between the conducting layer and the charge reservoir becomes closer so that the charge transfer process becomes easier and requires minimal energy, which causes superconductivity (T_c) to appear more easily. Therefore, at sample x = 0.15, superconductivity was observed with a T_c value of 11 K, whereas at x = 0.10, no trace of superconductivity was observed. From the magnetic susceptibility measurements, the paramagnetic characteristic was observed for x = 0.10, with no sign of a superconducting phase. Meanwhile, for samples with x = 0.15, diamagnetic characteristics can be identified in sample with y = 0. The onset of T_c was observed around 11 K, as indicated by a change in paramagnetic to diamagnetic characteristics. It can be seen that the superconductivity phase disappears in the sample with y = 0.01. The values of C, $n\mu^2$ and μ_{eff} for samples with x = 0.10 and y = 0 are larger than those of x = 0.15 and y = 0. Zn impurities caused the value of *C*, $n\mu^2$, and μ_{eff} decreased in both samples of x = 0.10 and x = 0.15. The decrease of magnetic parameters by Zn is probably due to the decrease of the amount of Cu²⁺ and the possible existence of the dynamical strip correlation of spin and charge. Changes in the value of magnetic parameters such as C, $n\mu^2$, and μ_{eff} by Zn impurity are expected to be used as the first indication of the existence of stripe-pinning model in electron-doped superconducting cuprates of $Eu_{2-x}Ce_xCu_{1-y}Zn_yO_{4+\alpha-\delta}$.

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