X-ray Absorption Studies on Cu–doped ZnO Nanoparticles Synthesized by Coprecipitation Method

D A Daratika 1, C Saiyasombat 2, K Kamonsuangkasem 2, M A Baqiya 1, and Darminto 1*

1 Department of Physics, Institut Teknologi Sepuluh Nopember (ITS), ITS Campus Keputih-Sukolilo, Surabaya 60111, Indonesia.
2 Synchrotron Light Research Institute, 111 University Avenue, Muang District, Nakhon Ratchasima 3000, Thailand.

*Email: darminto@physics.its.ac.id

Abstract. Copper–doped ZnO (CZO) nanoparticles have successfully been synthesized by coprecipitation method with Cu concentrations ranging from 0 to 5 wt%. The effect of Cu concentration on electrical properties and the oxidation state of ZnO were investigated. The x-ray diffraction (XRD) pattern analysis shows CZO phase formed with calcination at 400°C for 3 h. The crystal size of CZO nanoparticles, evaluated using MAUD software, is in the range of 56–90 nm. It was obtained that the Cu doping has reduced the optical band gap from 2.85 eV to 3.06 eV, while the electrical conductivity increased from 1.03 x 10⁻⁸ to 24.25 x 10⁻⁸ S/cm. The highest conductivity of CZO is achieved by the sample doped with 4 wt% Cu. This result has been further studied by the x-ray absorption near edge spectroscopy (XANES) measurement at Cu K-edge related to the oxidation state of the Cu ions substituting Zn sites.

1. Introduction
Zinc oxide (ZnO) is a transparent semiconductor oxide with a wide direct band gap (3.37 eV), a large exciton binding energy (60 meV) at room temperature, and chemically and thermally stable. Due to these properties, it has emerged as a promising material for gas sensor, memory of optical and magnetic devices, piezoelectric transducers, photodiodes, photodetectors, UV-light emitting diodes (UV-LEDs), biomedical, solar cell, and transparent conductive oxide. Nowadays, synthesis of ZnO nanoparticles can be done by using several methods including a ball milling, auto-combustion, sol-gel process, hydrothermal route, and co-precipitation method [1].

Various efforts have already been made to investigate the effect of doping transition metals like Cu, Co, Al, Li, Ni, Fe, etc. on its electrical, optical, and magnetic properties. Among these doping elements, copper (Cu) is a potential dopant to improve the electrical conductivity which has low resistivity (1.67 x 10⁻⁶ Ω cm), and has many physical and chemical properties that are similar to zinc (Zn), such as having a similar structure of the electron shells [2]. The presence of copper is used as a variable electrical conductance, thus it can control the electrical conductivity of ZnO. The Cu doping in ZnO changes the electrical properties but the effect of Cu in ZnO is debatable. There are many studies which have led to a number of hypotheses. Singhal, et al. (2012) have reported that Cu-doped ZnO (CZO) nanoparticles have Cu valence state of 2+ [2]. Suja et al. (2015) have found that CZO thin films have Cu valence state of 1+ [3]. Chakraborti et al. (2007) have reported that CZO thin films have mixed valence state of both Cu⁺ and Cu²⁺, which is also suggested that besides Cu²⁺ has substituted, the Cu⁺ lies in the interstitial sites [4]. The XANES is one of the x-ray absorption spectroscopy (XAS)
Figure 1. XRD patterns of Cu-doped ZnO (CZO) nanoparticles.

spectra region dominated by strong photoelectron scattering whose energy is located in the range of 40 eV above an absorption edge, and provides local information on materials such as oxidation state [5]. Sung et al. (2013) have reported the oxidation state of Cu in CZO thin films is 2+ determined by XANES measurements [6].

In the previous work, synthesis of CZO nanoparticles by coprecipitation has obtained that the Cu doping has reduced the optical band gap from 3.06 eV to 2.85 eV, while the electrical conductivity increased from $1.03 \times 10^{-8}$ to $24.25 \times 10^{-8}$ S/cm. The highest conductivity was achieved by the sample doped with 4 wt% Cu [7]. In this research, it will be studied further on this electrical conductivity of the CZO nanoparticles based on the oxidation state where Cu ions substituting Zn ions using XANES measurement at Cu K-edge.

2. Experimental Procedure
CZO nanoparticles have been synthesized by coprecipitation method with Cu concentrations ranging from 0 to 5 wt% (which is marked as CZO0 for the undoped ZnO, and CZO1, CZO2, CZO3, CZO4, CZO5, respectively) using zinc acetate dehydrate [Zn(CH$_3$COO)$_2$.2H$_2$O], and copper powder in certain compositions as raw materials, which were mixed and dissolved in an appropriate amount of 0.5 M HCl. The 0.5 M NH$_4$OH was gradually added to the solution by titration method to achieve pH around 9. The experimental procedure was similar with the previous work [7]. The crystal structure and phase of the samples were investigated using XRD with scanning angle 2θ ranging from 20° to 70° and operated at 40 kV and 30 mA with CuK$\alpha_1$ radiation with wavelength of 1.54 Å. The oxidation state where Cu has substituted Zn ions were investigated using XAS technique including XANES measurement at Cu K-edge, performed using synchrotron radiation at Synchrotron Light Research Institute (SLRI) using the beamline BL1.1W (Multiple X-ray Techniques) in Thailand.

3. Results and discussion
The phase purity and crystal structure of CZO nanoparticles for various doping concentrations have been studied by XRD patterns. Figure 1 shows the patterns of CZO nanoparticles. Diffraction peaks have been observed to be sharp implying high crystallinity of the samples. All samples show only reflection planes of ZnO phase indicating that Cu ions are dissolved into ZnO structure, so that Cu have substituted Zn ions without forming any impurity phases such as Cu$_2$O, and CuO. The XRD peaks show that CZO nanoparticles have wurtzite structure for all Cu concentrations.

The diffraction patterns were further analyzed by Rietica and MAUD (Material Analysis Using Diffraction) software using Rietveld method to evaluate the lattice parameter and crystallite size of the samples, respectively. The results of lattice parameters and crystallite size of CZO samples are tabulated in Table 1. Both of the lattice parameters and crystallite size decrease with the increasing concentrations of Cu. This indicates that Zn$^{2+}$ (0.74 Å) ions are successfully replaced by the Cu ions.

![XRD patterns of Cu-doped ZnO (CZO) nanoparticles.](image-url)
This result leads us for further investigation by XAS measurements at Cu K-edge to understand the information of Cu ions substituting the Zn sites. In the previous work, the Cu doping had been found to reduce the optical band gap from 2.85 to 3.06 eV, while the electrical conductivity increased from 1.03 x 10^8 to 24.25 x 10^8 S/cm. The highest conductivity was achieved by the sample with 4 wt% Cu doping [7]. Based on these results, it was expected due to the change of oxidation state of Cu ions and it may explain the highest conductivity phenomenon occurred in the sample with 4 wt% Cu doping.

Table 1. Crystallite size, and lattice parameters of Cu-doped ZnO (CZO) nanoparticles.

| Copper content (wt%) | Crystallite size (nm) | Lattice Parameter | Volume Cell |
|----------------------|-----------------------|-------------------|-------------|
| 0                    | 90                    | a = b (Å) | c (Å) | α = β (°) | γ (°) | 45.760006 |
| 1                    | 84                    | 3.207590 | 5.135677 | 90 | 120 | 45.759407 |
| 2                    | 76                    | 3.206976 | 5.134461 | 90 | 120 | 45.731655 |
| 3                    | 71                    | 3.206475 | 5.132681 | 90 | 120 | 45.701523 |
| 4                    | 62                    | 3.205377 | 5.133203 | 90 | 120 | 45.674858 |
| 5                    | 56                    | 3.205587 | 5.131305 | 90 | 120 | 45.663967 |

One of the most appropriate ways to determine the oxidation state of dopant atom is XANES measurement, analyzed by the Athena program. The XANES spectra at Cu K-edge for CZO nanoparticles (CZO3, CZO4, and CZO5) are shown in Figure 2 (a), and their derivatives in Figure 2 (b) along with the standard reference samples, which are Cu foil, Cu2O, and CuO with 0, +1, +2 oxidation states of Cu, respectively. The different concentrations of Cu affected the XANES spectra.

The most primary region in the XANES Cu-K edge spectra is absorption edge. The edge region is formed by the transition of electrons from the deep core to the unoccupied outer shell depending on the absorber atom used in XANES measurements. The transition of the edge for Cu K-edge is from 1s to 3d. The electron configuration of Cu^{1+} is [Ar] 3d^{10} 4s^{0}, and that of Cu^{2+} is [Ar] 3d^{9} 4s^{0}, while Cu^{3+} is [Ar] 3d^{8} 4s^{0}. The transition of electrons from the deep core on the K-edge are from the 1s orbital to the unoccupied orbitals. However, Cu^{+} and Cu^{2+} valence state does not have a hole in the 3d orbitals, so in this state, the transition of 1s to 3d is not allowed [6].

Figure 2 (a) shows the XANES Cu-K edge spectra of CZO nanoparticles (CZO3, CZO4, and CZO5) compared with the standard samples (Cu foil, Cu2O, and CuO). The absorption edge energy (E0) can be seen at the first peak of the XANES spectra which can be seen clearly using the first derivative in Figure 2 (b). The absorption edge energy positions of Cu reference were determined to be 8979 eV, 8980.14 eV, and 8983.58 eV for Cu foil, Cu2O, and CuO, respectively. The absorption edge energy shifts to a higher value when the oxidation state increases. The edge positions of Cu were at 8985.01 eV, 8985.12 eV, and 8984.71 eV for CZO3, CZO4, and, CZO5, respectively. The absorption edge position of CZO4 has the highest edge energy. The greater value of edge energy indicates more photons absorbed by Cu (as an absorber atom) which is characterized by the high absorption edge peak.

Previous research carried out by Kataoka et al. (2011) described that the CZO nanowires had mixed valence state of both Cu^{2+} and Cu^{3+}, where Cu^{2+} ions were dominant in the surface area [8]. Deng et al. (2016) showed that the Cu^{3+} in NaCu2O3 material had been measured using XANES with an edge energy position of around 8984 eV [9]. Based on the comparison between the CZO samples and Cu standard samples, the oxidation state of all samples was approximately 3+. This is due to the oxidation occurred in the samples during synthesizing the nanoparticles at relatively high temperature, and also because of high Cu concentration as the dopant.
Figure 2. (a) Cu K-edge XANES spectra, and (b) their first derivatives of Cu-doped ZnO (CZO) nanoparticles.

Based on the present results, it can be seen that the decreases of the lattice parameters and crystallite size of CZO nanoparticles were caused by Cu\(^{3+}\) ions successfully substituting on \(\text{Zn}^{2+}\) sites. It is caused by Cu\(^{3+}\) ions having the ionic radius less than that of Cu\(^{2+}\) ions (0.73 Å), since Cu\(^{3+}\) ion loses one electron compared with “normal” Cu\(^{2+}\) ion. The CZO with concentration of 4 wt% Cu (CZO4 sample) has the highest electrical conductivity [7]. It is probably because the CZO4 sample has the highest absorption edge energy so that the oxidation state is higher than other samples affecting the amount of charge carrier in the sample. Thus, it may reduce slightly the band gap of CZO nanoparticles.

4. Conclusion

The CZO nanoparticles have been successfully synthesized using coprecipitation method. XRD characterization shows that CZO nanoparticles have single phase of wurtzite structure with crystal size in the range of 56 – 90 nm. The decrease of the lattice parameters and crystallite size of CZO nanoparticles was caused by Cu\(^{3+}\) ions successfully substituting on the position of \(\text{Zn}^{2+}\) sites. The oxidation states of Cu in all samples, determined by XANES measurements, were around 3+. The CZO4 sample has the highest electrical conductivity. It is probably due to the highest absorption edge energy of CZO4 so that the oxidation state is higher than the other samples providing more electronic charge carriers.

5. References

[1] Al-Ghamdi A A, Al-Hartomy O A, El Okr M, Nawar A M, El-Gazzar S, El-Tantawy F, Yakuphanoglu F 2014 *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* 131 512
[2] Singhal S, Kaur J, Namgyal T, Sharma R 2012 *Phys. B. Condens. Matter* 407 1223
[3] Suja M, Bashar S B, Morshed M M, Liu J 2015 *ACS Appl. Mater. Interfaces* 7 8894
[4] Chakraborti D, Narayan J, Prater J T 2007 *Appl. Phys. Lett.* 90 062504
[5] Ankudinov A L, Ravel B, Rehr J J, Conradson S D 1998 *Phys. Rev. B* 58 7565
[6] Sung N-E, Kang S-W, Shin H-J, Lee H-K, Lee I-J 2013 *Thin Solid Films* 547 285
[7] Daratika D A, Baqiya M A, Darminto 2017 *IOP Conf. Ser. Mater. Sci. Eng.* 196 012009
[8] Kataoka T, Yamazaki Y, Singh V R, Fujimori A, Chang F-H, Lin H-J, Huang D J, Chen C T, Xing G Z, Seo J W 2011 *Phys. Rev. B* 84 153203
[9] Deng Y, Handoko A D, Du Y, Xi S, Yeo B S 2016 *ACS Catal.* 6 2473

Acknowledgment

This research was partially supported by “Hibah KLN”, Kemenristekdikti, Indonesia, 2017. The use of experimental facilities at Synchrotron Light Research Institute (SLRI), using beamline BL1.1W (Multiple X-ray Techniques), Thailand, was thankfully appreciated.