Comparation of X-ray diffraction pattern refinement using Rietica and MAUD of ZnO nanoparticles and nanorods

S. Y. Purwaningsih, N. Rosidah, M. Zainuri, T. Triwikantoro, S. Pratapa and D. Darminto
Department of Physics Institut Teknologi Sepuluh Nopember (ITS), Kampus ITS Sukolilo Surabaya 60111, INDONESIA
E-mail: yani@physics.its.ac.id, darminto@physics.its.ac.id

Abstract. ZnO nanoparticles and nanorods were synthesized using a simple co-precipitation method. X-ray diffractometry was used to investigate the purity and nanocrystallinity of the final powders. Rietveld refinements for x-ray diffraction data of the nanopowders have been done using Rietica and MAUD softwares. The study was to compare the adjusted parameters in the models where Voigt and pseudo-Voigt functions, respectively, are used as profiles adopted in the softwares. Refinements using Rietica gives Lorentzian and Gaussian peak broadening components and preferred orientation parameter. The peak broadening components can be used to estimate crystallite size and non-uniform microstrain. MAUD can directly give crystallite size and its distribution parameter, microstrain and preferred orientation value. Further study and investigation using scanning electron microscopy (SEM) are required to confirm the accuracy of the diffraction size results.

1. Introduction
Zinc oxide (ZnO) is a direct wide band energy gap semiconductor with \( (E_g = 3.37 \text{ eV} \text{ at } 300 \text{ K}) \) with a wurtzite structure. The most outstanding feature of ZnO is its large exciton binding energy (60 meV), which is about three times larger than that of ZnSe and GaN. Based on these characteristics, ZnO have potential technological applications such as light-emitting diodes (LEDs), solar cell windows, photo detectors, gas sensors and transparent conductive films [1]. Nanostructures like nanoparticles and nanorods have become the most promising research material because of their wide range of applications. The nano sized ZnO powder can be produced by various methods such as sol-gel [2], spray pyrolysis [3], hydrothermal/solvothermal [4], thermal evaporation [5], and co-precipitation [6, 7] from some kinds of precursors. From the literature, several works have been reported for the effective synthesis and characterization of ZnO nanoparticles and nanorods by co-precipitation technique [6, 7]. In this paper, a simple co-precipitation route was employed to produce zinc oxide nanoparticles and nanorods without using any calcination process, and then investigated using X-ray diffraction (XRD) analysis. The XRD spectra generally contain some information including the content of crystalline phase, crystallite size and shape of the phase, the crystallinity of products, and the growth orientation. All such informations are covered in the position, height, shape and width of the diffraction peaks [8]. To extract the XRD data needed further analysis by Rietveld method [9]. Rietveld method is a nonlinear fitting method between the curves of the calculated and the measured diffraction patterns based on the crystal structure data by the least squares method. This way is increasingly known widely supported by Rietica [10] and MAUD [11] softwares. This paper aims to report the refinement results of the diffraction patterns by using Rietica and MAUD on ZnO nanoparticles and nanorods.
2. Experimental Methods

2.1. Synthesis of zinc oxide nanoparticles
All of the chemical reagents used in the synthesis process were analytical grade and manufactured from Merck. The precursor solution was in the first step prepared using 2.2 g of zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) was dissolved in hydrochloric acid (HCl, 0.5 M) to prepare 0.5 M ZnCl₂ solution. The resulting solution was stirred for 1 h at room temperature to yield a homogeneous solution. Predetermined amount of ammonium hydroxide (NH₄OH) was dissolved in distilled water to prepare 0.5 M NH₄OH solution. Under constant stirring, 40 ml NH₄OH solution was added drop-wise at room temperature. The solution pH was adjusted to 9.5 by adding NH₄OH. After reaching pH-9.5, the colloidal solution was left stirring for 6 h at 85 °C temperature. At the end of the reaction, the white precipitate was collected by filtering and washed for several times by deionized water, and finally dried in a furnace at 100 °C for 3 h.

2.2 Synthesis of zinc oxide nanorods
To investigate the effect of the addition of the base solution during this process on morphology and particle size, in another experiment zinc oxide nanopowders was prepared following the same procedure as mentioned above except that injecting NH₄OH. The dropping of NH₄OH was performed just after the resulting solution heated to the growth temperature of 85 °C for the duration of the reaction for 1 h. The solution pH was also controlled to 9.0 with continuous stirring to yield precipitates of zinc hydroxide. The solution that formed with the dropping of NH₄OH to the zinc acetate solution was kept stirred for 6 h at the same temperature of growth. The white products were filtered, washed for several times with distilled water to remove ammonium acetate and dried in the manner as above.

2.3. Characterizations
The structural characterizations of the prepared samples were performed using X-ray powder diffraction analysis (XRD) on a Philips X’Pert MPD Diffractometer system equipped with Cu-Kα radiation (λ = 1.5406 Å) in the 2θ range from 20° to 70° working at 40 kV and 30 mA. Structural refinements using the Rietveld method were carried out using Rietica and MAUD programs; lattice parameters (a, c), cell volume (V), preferred orientation (PO), microstrain (ε) and crystallite size (D) were refined. The characterization by scanning electron microscopy (SEM) was performed with a FEI type inspect S-50 system.

3. Results and Discussion
The X-ray diffraction patterns of the synthesized ZnO nanoparticles and nanorods are shown in Figure 1. The XRD profile of the samples shows the characteristic peaks corresponding to planes (100), (002), (101), (102), (110), (103), (200), (112), and (201) indicates the formation of hexagonal wurtzite-type structure. These diffraction peaks are well indexed with the Joint Committee on Powder Diffraction Standards (JCPDS, card no.36-1451) [12]. It is evident from the XRD data that no extra peaks related to the organic residuals or other metal oxides is detected, which confirms that the obtained samples are of pure and single phase.

Figure 2(a) and (b) shows Rietveld refinements results of X-ray diffraction patterns with Rietica of nanoparticles and nanorods, respectively. Meanwhile Rietveld refinements were carried out using MAUD and the results are reported in Figure 3(a) and (b) for nanoparticles and nanorods, respectively. Table 1 shows the degree of fit (figures-of-merits - FoMs) of refinements of X-ray diffraction patterns with Rietica. Refinements with Rietveld method can be received from the criteria required by Kisi, i.e. GoF<4% and Rwp<20% [13]. Table 1 also shows the degree of fit of refinements with MAUD. Refinements with MAUD acceptable of the criteria required by Lutterotti, i.e. sig<2% and R_w<15% [11]. Based on Tables 1 indicating that Rietveld and MAUD refinements for all data have met the required criteria. Thus the refined parameters can be analyzed further.
Figure 1. X-ray diffraction profile of ZnO nanoparticles and nanorods.

Based on Table 2 it appears that the measured diffraction patterns are represented by the sign (+) and the calculated ones are represented by solid red curve. The bottom most curve is the plot of difference between the measured and the calculated diffraction patterns (solid green curve). The vertical blue line shows the peak positions of Bragg (l).

Figure 2. Rietveld refinements results with Rietica of samples produced with co-precipitation.

Figure 3. Rietveld refinements output plot using MAUD of samples. The measured diffraction data are shown by a (+) sign in blue, while the calculated ones by solid line in black. Vertical line represents the positions of diffraction lines for ZnO. The line below the vertical lines shows the difference profile between measured and calculated patterns.
Table 1. Fitting (FoMs) from Rietveld refinements with XRD data for ZnO samples determined with (a) Rietica, and (b) MAUD.

|                | Rietica | Nanoparticles | Nanorods | MAUD | Nanoparticles | Nanorods |
|----------------|---------|---------------|----------|------|---------------|----------|
| GoF            | 1.98    | 3.94          |          | 1.51 | 5.52          |          |
| $R_{wp}$ (%)   | 13.56   | 14.24         |          | 14.52| 42.40         |          |
| $R_p$ (%)      | 10.10   | 10.97         |          | 13.28| 48.92         |          |
| $R_{exp}$ (%)  | 9.63    | 7.18          |          | 10.69| 32.38         |          |

The structural parameters, preferred orientation, crystallite sizes and microstrain obtained from refinements are shown in Table 2. The number in brackets shows the standard deviation of the last significant digit. The calculated lattice parameter values for each sample in each refinement with XRD data are approximately 0.3256 nm ($a = b$) and 0.5215 nm ($c$) for nanoparticles sample, while for nanorods sample gives result about 0.3213 nm and 0.5147 nm. Meanwhile, for the standard lattice parameters of ZnO are 0.3249 nm ($a = b$) and 0.5206 nm ($c$). The cell volume of ZnO nanoparticles and nanorods was calculated from Rietica and the results are 47.8779 and 46.0196 nm³, respectively. Meanwhile, the average crystallite size was estimated by using MAUD for samples are approximately 42 and 148 nm, respectively.

Table 2. Output of the Rietveld refined XRD data analysis obtained by Rietica and MAUD.

| Sample      | Lattice parameters | Cell volume | Preferred orientation | Crystallite size | Microstrain |
|-------------|--------------------|-------------|-----------------------|------------------|-------------|
|             | $a = b$ (nm)       | $c$ (nm)    | ($nm^3$)              | (nm)             | (%)         |
| Nanoparticles | 0.3256             | 0.5215      | 47.8779               | 0.9835           | 42(2)       | 0.027(5)    |
| Nanorods    | 0.3213             | 0.5147      | 46.0196               | 1.0083           | 148(15)     | 0.006(5)    |

Figure 4. Crystal size distribution profile with XRD data for samples.

The difference of both the softwares were caused by two things, namely (i) the contribution of the effect of size on the selected peak shape functions, (ii) the effect of crystal size distribution. In Rietica, for the effect of size only contributes to the variance of the Lorentzian function on the selected Voigt function [14]. While in MAUD, the effect is taken on the variance of two peak shape functions, namely Lorentzian and Gaussian. Furthermore, the effect of crystal size distribution [15] is not available for Rietica, whereas in MAUD of the crystal size distribution is obtained as shown in Figure 4. With the availability of the structural data and crystal size distribution, MAUD becomes more appropriately used for the microstructural analysis (or nanostructure) and its distribution, especially for the characterization of nanomaterial sizes. In addition, the superiority of MAUD is the peak widening correction by the instrument can be done in an integrated with the refinement of parameters in it.
Figure 5. SEM images of ZnO nanoparticles and nanorods.

Figure 5 presents SEM images of ZnO nanoparticles and nanorods. The presence of agglomerated ZnO particles or some bigger particles for ZnO in Figure 5(a) could be attributed to the overlapping of smaller particles. The average diameter of the particles that can be seen in these images is 40 nm. Fig. 5(b) show nanorod of ZnO where the measured diameter is 0.9 μm and length is 5.7 μm. These sizes are in good agreement with particle size as described in Table 2. Therefore it concluded that the presence of adding base has a significant influence on the structure and morphology of ZnO product.

4. Conclusions
ZnO nanoparticles and nanorods were succesfully synthesized by co-precipitation method. Rietveld analysis confirms the formation of pure phase. The refinements of the X-ray diffraction patterns using Rietica and MAUD may provide information on the microstructural information of ZnO nanoparticles and nanorods from the co-precipitation results. The estimated crystallite size according to MAUD can be said to be more representative with the parameter of crystal size distribution than according to Rietica.

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6. References

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