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Visualization and simulation of ZnO microstructure with various crystal structures and doping compositions based on XRD patterns using VESTA

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ABSTRACT

Crystal structure visualization and X-ray diffraction pattern simulation of various types of ZnO microstructures have been successfully carried out using the VESTA software program. The purpose of this study was to obtain the relationship between the shape of the structure, microstructure, and composition to changes in the pattern and peak diffraction. The software program produces information on the shape of the crystal structure and representative X-ray diffraction patterns for ZnO microstructures. This program requires input in the form of coordinates of each constituent atom, lattice parameters, and spatial symmetry. The output obtained is a graph of the diffraction pattern and crystal structure that provides an overview of the profile and type (phase) of the ZnO microstructure. The results showed that the peak position and intensity of the diffraction pattern were influenced by the arrangement of atoms in the unit cell. In variations in structure and microstructure, the position of the diffraction peak provides a different picture for each type of structure depending on the arrangement of atoms in the unit cell, where each crystal structure has a different position and spatial symmetry, resulting in different diffraction patterns. The nanorod structure has a monoclinic crystal system ($a \neq b \neq c$) with a space group of C 2 / c and lattice parameters a = 15.4170 Å, b = 25.3560 Å, and c = 14.3840 Å. The nanowire structure has a triclinic crystal system ($a \neq b \neq c$) with lattice parameters a = 12.0380 Å, b = 2.4910 Å, c = 16.8890 Å and a space group of P-1 and is the simplest form of symmetric lattice. The nanoflower structure has an orthorhombic crystal system ($a \neq b \neq c$) with lattice parameters a = 9.47310 Å, b = 13.52960 Å, c = 29.0220 Å and space group P b c a.

Keywords: RIETAN-FP; simulation; VESTA; visualization; X-ray diffraction

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INTRODUCTION

Zinc oxide (ZnO) nanoparticles are one of the most widely used n-type semiconductor metal oxide materials due to their multifunctional morphological, photonic, and spintronic properties. This is characterized by a wide direct band gap of 3.37 eV and a high excitation energy of 60 meV. ZnO is widely used because of its characteristics [1].

The characteristics of the material structure are very important to know to analyze materials. The crystal structure of a material is closely related to the properties of the material. The properties of the material are built on two main concepts, namely the concept of the atomic structure of the crystal and the concept of material treatment. The concept of material treatment explains the interactions between atoms and changes in atomic structure. Knowledge of the crystal structure of a material can indirectly provide information on the properties of the material [2].

The crystal structure can be determined manually or with a computer program based on the X-ray diffraction pattern. Determination of the crystal structure manually is done by determining the lattice constant, the adopted space group, and the position of the atoms in the crystal unit cell based on X-ray Scattering data. However, sometimes problems arise when different atoms and very close atomic numbers have almost the same scattering so that their peaks overlap. Therefore, experts try to develop computer analysis methods to interpret the structure of the crystal based on Bragg's Law.

The advantage of using a computer program for analysis is that calculations can be done faster, saving time and the final results given by the computer are also reliable. The structural analysis that is often done is based on structural refinement using the Rietveld method [3].

The depiction of crystal structures is still very rarely reported. Simulation of X-ray diffraction patterns of various natural zeolite minerals has been carried out by [4]. The simulation results in the form of diffraction pattern profile graphs and crystal structure data information that were carried out showed significant and representative results from the seven zeolite phases simulated in previous studies by simulating X-ray diffraction patterns with the RIETAN-FP program. Visualization of crystal structures and simulation of X-ray diffraction patterns using VESTA have been carried out by [5], using perovskite $Ba_{1-x}Sr_xTiO_3$ ceramic crystals as the object of their research. The results of the study indicate that the peak position and intensity of the diffraction pattern are influenced by the arrangement of atoms in the unit cell. The addition of impurity atoms such as Sr on the Ba side in $BaTiO_3$ causes changes in the structure of $BaTiO_3$.

In this study, visualization of various ZnO crystal microstructures will be carried out using software by simulating X-ray diffraction patterns using the VESTA and RIETAN-FP software programs. The material targeted for the study is the ZnO microstructure. The visualization and simulation carried out were made with three different categories of variations including structural variations, composition variations, and microstructure variations. Based on the visualization of the ZnO microstructure obtained, it is expected to be used as a reference for research in analyzing the structure of materials whose crystal structure is not yet known.

LITERATURE REVIEW

Zinc Oxide (ZnO)

ZnO is an inorganic semiconductor that is generally in powder form and is non-toxic and has high electron mobility and thermal stability. ZnO is a semiconductor formed by a combination of group IIB (element Zn) and VIA (element O) groups. Its ionization energy lies between ionic semiconductors and covalent semiconductors [6].

Like most group II-VI materials, the ZnO bond is ionic ($Zn^{2+} – O^{2-}$) with a radius of 0.074 nm for Zn^{2+} and 0.140 nm for O^{2-}. This property explains the preferential formation of a hexagonal structure rather than zincblende and the strong piezoelectric properties of ZnO are caused by the polar Zn–O bond, where the zinc and oxygen planes are electrically charged.

ZnO has a structure that can crystallize into three main forms, namely wurzite, zincblende and rocksalt [7]. The cubic rocksalt structure has cubic crystals with lattice parameters a = b = c = 4.1440 Å and space group F-m3m. The diffraction pattern of cubic rocksalt ZnO produces maximum peak intensity at the three highest peaks I (200) > I (220) > I (111). The cubic rocksalt structure is formed at high temperatures. The ZnO structure in the form of cubic rocksalt has a band gap energy of 2.7 eV with a lattice constant between 4.271 – 4.294 Å. The structure of zinc blende is one of the various structures produced from ZnO semiconductor material, with characteristics where the sides are not the same as each other. In general, the zinc blende structure is formed at high pressure and high temperature conditions which have lattice parameters a = b = c = 5.39 Å and space group F43m. The wurtzite structure is the most thermodynamically stable ZnO crystal structure. The ZnO phase has a hexagonal crystal structure (space group P63mc) with lattice parameters a = b = 3.246 Å and c = 5.198 Å, $\alpha = \beta = 90^o$, and $\gamma = 120^o$.

Crystal Structure

The properties and characteristics of solids are determined by the crystal structure contained in the material. Crystals are a type of atomic structure in which atoms are regularly and periodically (repeatedly) arranged in a

three-dimensional arrangement. Each atom is bound to each other at the closest distance to each other. The basic pattern or pattern of the crystal structure can be shown in a simple form called a lattice. The lattice is the position of the atoms that form the crystal. The periodic lattice arrangement forms a three-dimensional crystal system or crystal structure.

The concept of the Bravais lattice is used to formally define the crystal arrangement and its boundaries (limited). Crystals consist of one or more atoms, called bases or motifs, at each lattice point. The basis can consist of atoms, molecules, or strings of solid polymers, and the lattice provides the location of the basis.

Currently, there are only 7 types of crystal systems and 14 Bravais lattices [8] which are classified based on the number of crystal axes, the location of the crystal axes in relation to each other, the parameters used for each crystal axis and the number of space groups adopted. The seven crystal systems are as shown in Table 1.

Table 1. Crystal systems, lattice parameters, Bravais lattices and number of space groups.

Crystal system	Lattice parameters	Bravais lattice	Number of room groups
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	P	2
Monoclinic	$a \neq b \neq c$ $\alpha = \beta = 90° \neq \gamma$	P, C	13
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	P, I, C, F	59
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$	P, I	68
Cube	$a = b = c$ $\alpha = \beta = \gamma = 90°$	P, I, F	36
Rhombohedral / Trigonal	$a = b = c$ $120° > \alpha = \beta = \gamma \neq 90°$	R	25
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90°, \gamma = 120°$	P	27

X-Ray Diffraction (XRD)

XRD is a method used to determine crystal structure, phase changes and degree of crystallinity. X-ray diffraction by atoms arranged in a crystal will produce different patterns depending on the configuration formed by the atoms in the crystal [9].

The principle of XRD is based on X-ray diffraction, scattering of light with a wavelength of λ when passing through a crystal lattice with an angle of incidence of θ and a distance between crystal planes of d (Figure 2.3). The data obtained from the XRD characterization method are the scattering angle (Bragg angle) and intensity. Based on diffraction theory, the diffraction angle depends on the width of the lattice gap (distance between lattices) so that it affects the diffraction pattern, while the intensity of the diffracted light depends on how many crystal lattices have the same orientation.

The basic principle used to determine the crystal system is by using the Bragg's law equation:

$$2d \sin\theta = n\lambda \quad (1)$$

where, d is the distance between the lattice planes, θ is the measurement angle, n is the index, while λ is the wavelength of the X-ray.

The height of the diffraction peak on the Miller Index is determined by the ratio of the wavelength of the light to the distance between the crystal planes. The greater the difference between the refractive index value of the crystal and the refractive index value of the surrounding media, the shorter the wavelength of the light, so the higher the diffraction peak on the Miller Index. The greater the distance

between the crystal planes, the shorter the wavelength of the diffraction that will occur, so the higher the diffraction peak on the Miller Index. Therefore, the determinants of the height of the diffraction peak on the Miller Index are the refractive index value of the crystal and the distance between the crystal planes. In all crystal systems except the hexagonal crystal system, the crystallographic planes are determined using three Miller Indices, namely (hkl). Every two parallel planes have identical similarities and indices.

The hexagonal lattice parameters a and c are determined by calculations using the Cohen method based on the distance data between the crystal planes, d_{hkl}, obtained from the XRD peaks. For hexagonal structures using:

$$d_{hkl}^{-2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2} \quad (2)$$

Rietveld Analysis

The Rietveld method is a method published by Rietveld in 1967 to analyze diffraction patterns whose peaks overlap using the least squares principle. The Rietveld method can now be used to analyze neutron diffraction patterns and XRD on single crystal and polycrystalline samples. This method can also be used as a tool to characterize crystalline materials to extract various chemical and microstructural information, for example, analyzing phase composition and determining lattice parameters accurately [10].

Rietveld method software that can be used to analyze crystal structures includes XRS-82 (The X-rays Rietveld System-82). FullProf, RIETAN-FP and GSAS (general structure analysis system) software can be obtained from the internet for free and can be operated on a personal computer using the disk operating system (DOS) or Unix operating system.

VESTA

VESTA is a three-dimensional visualization system in the C++ programming language based on OpenGL technology for electronic and structural analysis developed by Koichi Momma and Fujio Izumi during 2001 – 2004. 3D visualizations that can be done include structural models, volumetric data ("voxel" data), and crystal morphology. Objects such as atoms, bonds, coordination polyhedra, isosurfaces can be rotated, scaled, and translated quickly in three dimensions. The scalability of VESTA is very high which allows it to handle an almost unlimited number of impractical objects such as atoms, bonds, polyhedra and polygons on isosurfaces as long as the memory capacity is sufficient. The image boundary is defined by the range along the x, y and z axes and the lattice plane [11].

VESTA can display crystal structures such as ball and stick, space-filling, polyhedral, wireframe, stick, and thermal-ellipsoid models with a variety of coloring features that indicate the quantity of each point on the surface. VESTA can be run on Microsoft Windows, Mac OS X, and Linux. The VESTA software program can handle multiple data in the same window, using a "tabbed" user interface. VESTA also supports multiple windows, each containing multiple tabs corresponding to files. VESTA can read files in 36 formats such as CIF, ICSD, and PDB and output files in 11 formats such as CIF and PDB.

VESTA can be directly connected to RIETAN-FP so that powder diffraction patterns can be simulated easily. Selecting the "Powder Diffraction Pattern" item under the "Utilities" menu causes a series of procedures to be run by VESTA as if they were implemented in VESTA such as the creation of input files, * .ins for RIETAN-FP, the execution of RIETAN-FP, and the graphical representation of the resulting data in * .itx files with graphic programs such as Igor Pro and gnuplot.

VESTA acts as a mediator between structural analysis and electronic structure calculations. All the advanced features and high performance contained in the VESTA software program are expected to contribute greatly to crystal and electronic structure investigations.

Crystal structures are visualized by placing atoms at specific positions in the unit cell. These positions are usually expressed in fractional coordinates (u,v,w), which are related to Cartesian coordinates by a transformation, e.g. r = (x,y,z) is the atomic position in Cartesian coordinates, r_frac = (u,v,w) is the position in fractional coordinates. Then the relationship between the two is:

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{matrix} a & b\cos(\gamma) & c\cos(\beta) \\ 0 & b\sin(\gamma) & c\dfrac{\cos(\alpha)-\cos(\beta)\cos(\gamma)}{\sin\gamma} \\ 0 & 0 & \dfrac{cV}{} \end{matrix} \begin{pmatrix} u \\ v \\ w \end{pmatrix} \quad (3)$$

where, V is the volume of the unit cell given:

$$V = \sqrt{1-\cos^2(\alpha)-\cos^2(\beta)-\cos^2(\gamma)+2\cos(\alpha)\cos(\beta)\cos(\gamma)} \quad (4)$$

VESTA also utilizes crystal symmetry elements, such as rotation axes, mirrors, and inversion centers, which are described using symmetry matrices. These symmetries are important in determining the repetition of crystal structures in space.

RIETAN-FP

The RIETAN-FP simulator program was created by F. Izumi and Y. Hamaguchi and installed on a Macintosh Computer. The method used is structural analysis with the Rietveld technique by entering two types of data, namely crystal structure parameter data and intensity. Crystal structure parameter data is input data for a proposed calculation model, while intensity data comes from the X-ray diffraction intensity of a sample. For simulation analysis, intensity data from XRD does not need to be entered. The results of the RIETAN-FP program processing will provide information in the form of structural parameter data, calculated intensity data and diffraction pattern profiles.

The RIETAN-FP simulation process is carried out by assuming that each type of phase has its own lattice parameters, space groups, and atomic positions in the unit cell as input data. Complete data on crystal structure parameters are taken from the JCPDS database, which is a collection body for X-ray diffraction experimental data from various sources whose origins and data accuracy can be traced. This database can be found in software which is an easy-to-use software for phase identification from powder diffraction data. In the MATCH!4 software there is a database containing various reference patterns.

RESEARCH METHODS

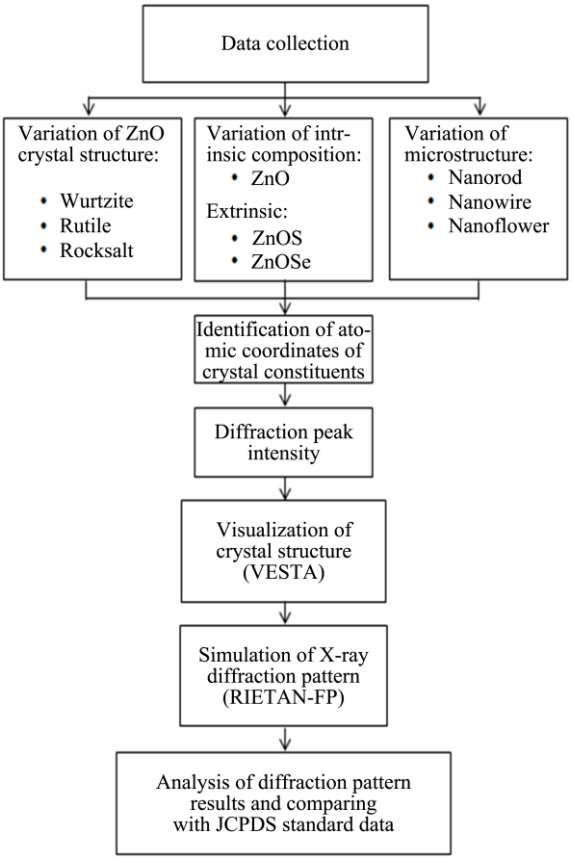
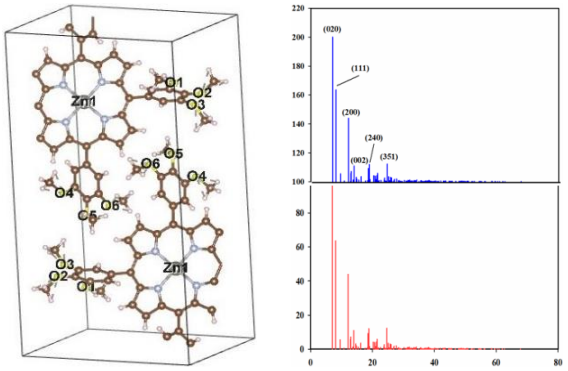


Figure 1. Research flow diagram.

Visualization was performed using VESTA Software with variations in crystal structure (wurtzite, rutile and rock salt), atomic composition (ZnO, ZnO;S and ZnO;Se) and microstructure (nanorod, nanowire and nanoflower). The visualization results were then simulated to obtain the diffraction pattern. The diffraction pattern was then compared with real data and the simulation results were analyzed in the form of crystal lattice parameters, structural shape, and diffraction peak positions.

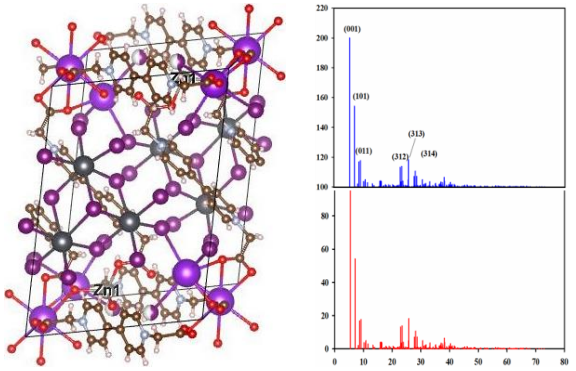
RESULTS AND DISCUSSION

Crystallographic Data



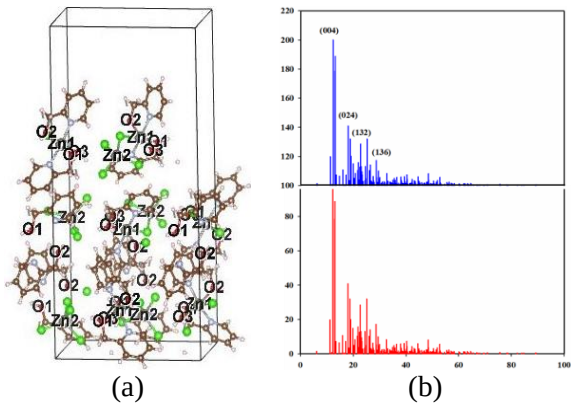
(a) (b)

Figure 2. (a) Visualization of the nanorod crystal microstructure and (b) its diffraction pattern.



(a) (b)

Figure 3. (a) Visualization of the nanowire crystal microstructure and (b) its diffraction pattern.



(a) (b)

Figure 4. (a) Visualization of the nanoflower crystal microstructure and (b) its diffraction pattern.

The discussion in this chapter presents the results of the crystal microstructure visualization and simulation of X-ray diffraction patterns of ZnO. The results of the crystal microstructure visualization for variations in composition and the shape of the X-ray diffraction pattern can be seen as follows Figure 2, 3, and 4.

Based on Figure 2, 3, and 4 above, the first column displays the visualization of the shape of the atomic structure that makes up a unit cell. The second column is a comparison of the diffraction pattern from the simulation with the JCPDS standard pattern from each crystal structure. The diffraction pattern shows that the peaks from the simulation match the peaks from the reference data in the JCPDS standard.

The nanorod structure has a monoclinic crystal system (a≠b≠c) with a space group C 2/c and lattice parameters a= 15.4170 Å b= 25.3560 Å c= 14.3840 Å producing maximum peak intensity with three highest peaks at I(020) > I(11-1) > I(200). The nanowire structure has a triclinic crystal system (a≠b≠c) with lattice parameters a= 12.0380 b= 2.4910 Å c= 16.8890 Å and a P-1 space group as in the picture which has 3 primary symbols and is the simplest form of symmetric lattice that produces maximum peak intensity with three highest peaks, namely I(001) > I(010) > I(001). The nanoflower structure has an orthorhombic crystal system (a≠b≠c) with lattice parameters a= 9.47310 Å b= 13.52960 Å c= 29.0220 Å and space group P b c a as shown in the figure which is included in the simplest symmetry lattice and produces maximum peak intensity with three highest peaks, namely I(004) > I (020) > I(112). Comparison of simulation lattice parameter prices with references can be seen in Table 2.

The positions of all diffraction peaks obtained from the simulation results are in accordance with the reference data for all structures that have been visualized. Each structure provides a different diffraction pattern according to the arrangement of atoms in the unit cell, spatial symmetry and field strengthening of each. This is in accordance with the theory of interaction and scattering of X-rays in crystals which states that the intensity of X-rays scattered by a crystal is determined

by the position of the atoms in the unit cell and the field strengthening (hkl) of the X-ray reflection, where each atom provides different electron scattering for each plane. Based on the data obtained with the reference, the visualization of a crystal structure can be tested for accuracy using this software so that it can be used to interpret XRD data correctly.

Table 2. Comparison of simulation lattice parameter prices with references.

Senyawa	Struktur	Parameter kisi	
		Referensi	Simulasi
Nanorod	Monoclinic *C 2/c*	a = 25.3330 Å b = 6.29900 Å c = 15.1610 Å	a = 15.4170 Å b = 25.3560 Å c = 14.3840 Å
Nanowire	Triclinic *P-1*	a = 18.9915 Å b = 18.9915 Å c = 12.5935 Å	a = 12.0380 Å b = 12.4910 Å c = 16.8890 Å
Nanoflower	Orthorhombic *P b c a*	a = 9.74700 Å b = 9.75100 Å c = 7.68900 Å	a = 9.47310 Å b = 13.5296 Å c = 29.0220 Å

CONCLUSION

In the variation of structure and microstructure, the position of the diffraction peak gives a different picture for each type of structure depending on the arrangement of atoms in the unit cell, where each crystal structure has a different position and spatial symmetry resulting in different diffraction patterns. The difference in the data value of the angle 2θ from the simulation results with the reference data is 0%, then the difference in the data value of the intensity of the simulation results with the reference is 8.87%.

Analysis of the simulation results in the form of crystal lattice parameters, structural shapes and diffraction peak positions shows that in the variation of structure and microstructure, the position of the diffraction peak gives a different picture for each type of structure depending on the arrangement of atoms in the unit cell, where each crystal structure has a different position and spatial symmetry resulting in different diffraction patterns. In the variation of composition, the ZnO compound has a hexagonal structure and its structure tends to change to monoclinic when added with S doping and its structure changes again to orthorhombic when doped with Se.

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