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Effect of Strontium Metal Doping on Crystal Structure and Band Gap Energy of Zinc Oxide Nanoparticles

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Abstract

Nanotechnology is a basic science that discusses the relationship between size, dimensions, and physical properties of nanostructured materials. This study aims to determine the effect of strontium administration on the crystal structure of ZnO nanoparticles. In this study, zinc oxide (ZnO) was doped with strontium using the coprecipitation method. The basic ingredients used are zinc chloride, strontium chloride, HCl solution, and NaOH precipitating solution. Variations in the concentration used for strontium doping are 0%, 3%, 5%, and 7%. The characterization was carried out by testing with XRD to determine the crystal structure, and UV-Vis to determine the band gap in the ZnO material. The results of the XRD diffraction test showed that the crystal structure of the sample was wurzite and orthorhombic. The crystal size was calculated using the Scherrer equation, and the crystal sizes obtained varied, namely ZnO of 101.28 nm, 3% of 61.19 nm, 5% of 94.91 nm, and 7% of 82.73 nm. The results of the characterization of the energy gap measurements carried out using the Tauc Plot method show that the application of strontium doping to ZnO nanoparticles causes a decrease in the value of the energy gap.

Keywords: Zinc Oxide, Strontium metal, Nanoparticles, Coprecipitation, Band Gap Energy

Introduction

Zinc Oxide (ZnO) has received special attention from researchers because it has interesting properties and many applications (Jiang et al., 2023);(Mirzaei & Darroudi, 2017). ZnO has a large band gap of 3.37 eV and an exciton binding energy of 60 meV at room temperature, high piezoelectric constant and high chemical stability (Liang et al., 2016);(Sangeetha et al., 2015). Its interesting properties make it a promising material for various applications such as ultraviolet light emitting diodes, solar cells, photo detectors, spintronic devices, biological sensors and photo catalysts (Karthika & Ravichandran, 2015);(El-Shazly et al., 2016).

Different synthesis methods have been widely used to synthesize ZnO nanostructures such as coprecipitation method, sol-gel method, hydrothermal method [6], solid state and wet chemical method (Ungula & Dejene, 2016);(Saleh et al., 2017);(Shatnawi et al., 2016). One of the simple, low-cost and effective synthesis methods used is the coprecipitation method used in the study to synthesize undoped and doped ZnO nanopowders (Belkhaoui et al., 2019);(Kareem et al., 2022).

Doping is an effective and efficient way to change the physical properties, especially optical, magnetic and electrical properties of the material to suit the needs and expand the application of the material from its basic properties (Zheng et al., 2022). To improve the photocatalytic ability of ZnO material, it is necessary to change the physical properties by doping metals, non-metals or noble metals (Arshad et al., 2013).

For example, optical and electrical supports can be improved by doping Group III elements in the periodic system such as Aluminum (Al), Gallium (Ga) and Indium (In) (Kim et al., 2014). Aluminum (Al) doping in ZnO can significantly cause the seed to have a morphology that increases the area of the layer wound and is useful for the efficiency of photocatalytic activity. Likewise, Strontium (Sr) doping is one that is suitable for inclusion in the ZnO lattice because it has high solubility to ZnO. Several studies have discussed the study of the effect of manganese doping on different properties of ZnO (Fabbiyola et al., 2016). Therefore, it is important to conduct research that focuses on the crystal structure and optical properties of ZnO nanoparticles doped with Strontium (Sr) material synthesized by coprecipitation method.

Research Method

The chemicals used in this study were zinc chloride ($ZnCl_2$) and strontium chloride ($SrCl_2$). The synthesis of ZnO and $Zn_{(1-x)}\ Sr_xO$ (x=0.00, 0.03, 0.05 and 0.07) nanoparticles was carried out using the coprecipitation method. For the synthesis of ZnO nanoparticles, the appropriate amount of $ZnCl_2$ powder was dissolved in 0.5 M HCl at room temperature with stirring using a magnetic stirrer for 5 hours. Then the titration process was carried out at room temperature with NaOH solution added dropwise so that the pH value reached 8.

The solution obtained was then stirred using a magnetic stirrer for 5 hours until it precipitated. The precipitate was separated from the solution by filtration and washed several times with distilled water. Then the precipitate was dried in an oven for 6 hours at a temperature of 100 ^oC and calcined for 2 hours at a temperature of 600 ^oC. All samples were synthesized through the same process. From the XRD test, data was obtained in the form of intensity values generated from each angle 2θ which had been set from 20° to 80°. The data results were then analyzed using Highscore Plus software to obtain the crystal size value. To calculate the crystal size value, the Scherrer formula is used:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where λ is the X-ray wavelength, θ is the diffraction angle. K is a constant that depends on hkl, β is the definition of the quantity used. The energy gap of the sample was obtained by characterizing it using Ultra Violet Visble (UV Vis). This test was conducted with the aim of obtaining initial data used to calculate the energy gap value using the following Kubelka-Munk equation:

$$[(F(R)h\nu]^{\gamma} = A(h\nu - E_g) \quad (2)$$

Where F(R) is the Kubelka-Munk function which is the ratio of the absorption coefficient and the scattering coefficient, while γ is the value of ½ for the indirect band gap and 2 for the direct band gap. The energy gap can be obtained by drawing a graph $(F(R)hv)^2$ of the function of hv.

Resulth and Discussion

Structural Analysis

In the test conducted using XRD, an X-ray diffraction pattern was obtained from the $Zn_{(1-x)}Sr_xO$ (x= 0.00, 0.03, 0.05 and 0.07) nanoparticles. The results of the XRD test were then analyzed to obtain the 2θ and FWHM values of the crystalline phase peaks seen and analyzed using Highscore software. From the data analysis of each sample using the Scherrer method, the crystallite size data was obtained from the XRD data. Table 1 shows the crystallite size results from each sample.

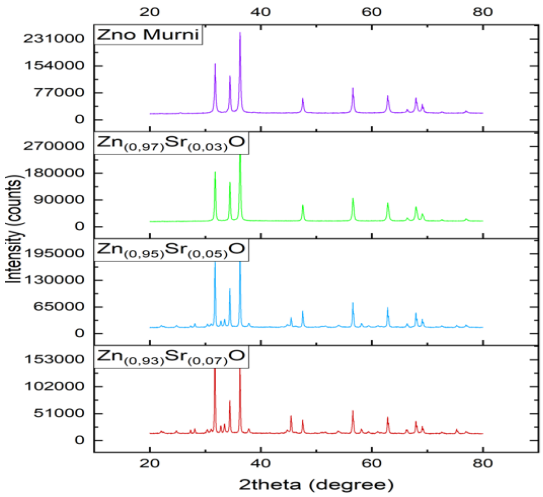

Fig. 1. X-ray diffraction pattern of Strontium-doped ZnO nanoparticle

After quantitative analysis using High Score software, it can be seen that the $Zn_{(1-x)}Sr_xO$ (x = 0.00, 0.03, 0.05 and 0.07) nanoparticles have different crystallite sizes. The crystallite size of pure ZnO is 101.28 nm, but there is a decrease in crystallite size of 61.19 nm at a dopant concentration of 3% and an increase in crystallite size of 94.91 nm at a dopant concentration of 5%, but a decrease in crystallite size again at a dopant concentration of 7% by 82.73 nm. According to Karthick and Sakthivel (2021), the decrease in crystallite size is caused by an increase in the concentration of Strontium doped in ZnO nanoparticles.

Band Gap Energy Analysis

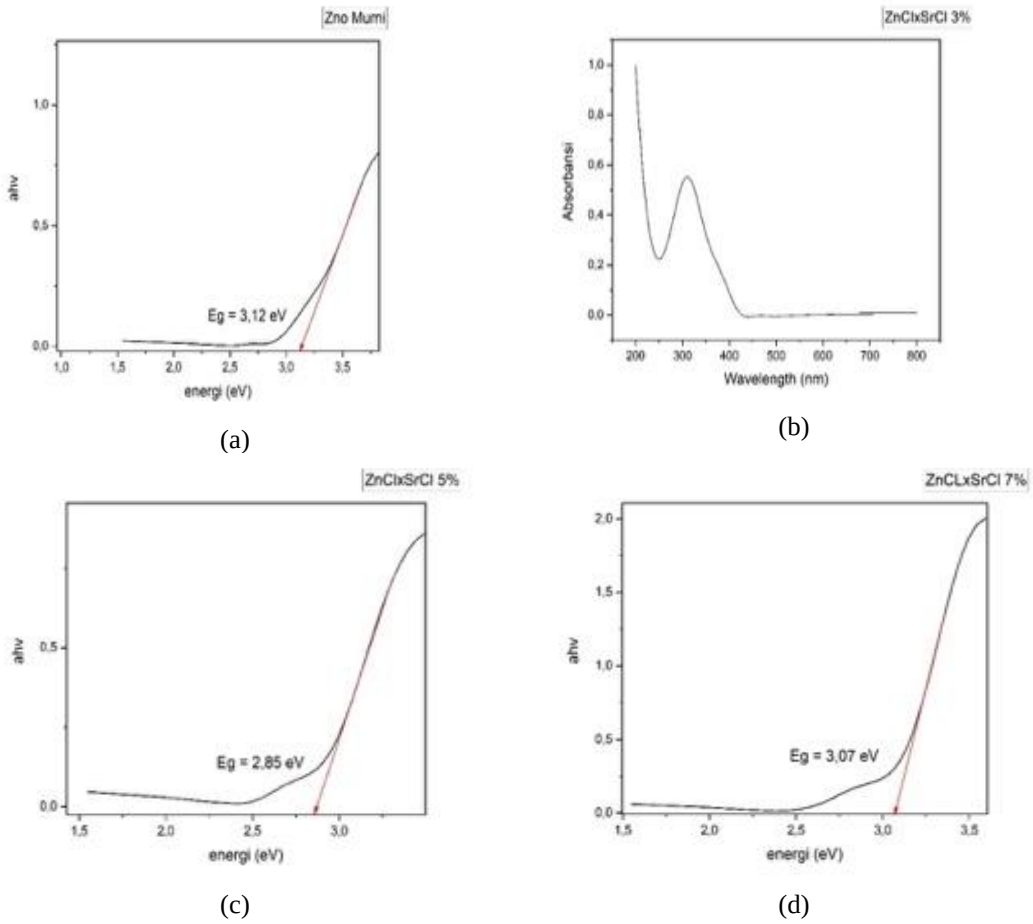

Fig.2. Band gap energy of $Zn_{(1-x)}Al_{0.02}Sr_xO$ nanoparticles :
(a) x=0.00; (b) x=0.03; x=0.05 and (d) x=0.07

UV-Visible characterization was carried out on ZnO nanoparticles doped using Strontium to see changes in UV-Visible radiation absorption related to optical properties. The results of UV-Visible characterization which were processed using the Kulbecka Munk method and the Tauc's Plot principle obtained results as in Fig. 2. In the Bulk state, ZnO has an energy gap value of 3.37 eV in Ultra Violet absorption conditions. After doping using Strontium, changes in the energy gap were obtained successively 3.12 eV, 3.06 eV, 2.85 eV and 3.07 eV. In conditions without doping, ZnO nanoparticles have an energy gap of 3.12 eV.

This decrease in energy gap is related to the shrinking of particle size from bulk conditions to nanoparticles with an average size of 101.28 eV. The decrease in the gap energy due to the annealing process is inseparable from the quantum confinement effect on semiconductor nanoparticles. In the Bulk state, the band gap structure is continuous, but when the particle size is smaller than the wavelength of the radiation energy, there is a change in the band gap energy level which becomes discrete. This causes the band gap to narrow.

Table 1. Crystal size and gap energy of Strontium doped ZnO nanoparticle samples

Nanoparticles	Crystallite sizw(nm)	Band gap energy (eV)
ZnO	101,28	3,12
$Zn_{0,97}Sr_{0,03}O$	61,19	3,06
$Zn_{0,95}Sr_{0,05}O$	94,91	2,85
$Zn_{0,93}Sr_{0,07}O$	82,73	3,07

One of the important factors that characterizes this study is the use of Strontium as a dopant in the main crystal structure of ZnO. Strontium is an element categorized as an n-type dopant that contributes many electrons. Electrons generated from the interstitial process of ZnO atoms and oxygen vacancies due to crystal defects directly affect the electrical conductivity. The electronic state of strontium 5s appears at a lower energy than Zn 4s which causes a narrowing of the band gap. This makes it easier for electrons to excite from the ground state to the excited state. The more Strontium doping, the narrower the energy band gap.

This is confirmed by the results of the energy gap calculation that the greater the Strontium dopant, the lower the energy gap. The lowest condition occurs when ZnO nanoparticles are doped with 5% Strontium. This concentration reduces the energy gap to 2.85 eV. However, at higher concentrations there is a different tendency. At 7% Strontium doping, the energy gap increases to 3.07 eV. This is in accordance with research conducted by Mohadeseh that the addition of intense doping to ZnO nanoparticles will cause the Burstein-Moss phenomenon where the valence band gap conditions that are heavily doped with n-type elements will cause the Fermi energy level to increase.

Conclusion

Strontium doping of ZnO nanoparticles results in a decrease in cryst al size. The crystal structure formed in the $Zn_{(1-x)}\ Sr_xO$ (x=0.00, 0.03, 0.05 and 0.07) is hexagonal wurzite. Strontium doping of ZnO nanoparticles causes a decrease in the energy gap value of $Zn_{(1-x)}\ Sr_xO$ (x=0.00, 0.03, 0.05 and 0.07). This occurs because of the interaction of p-d spin exchange between band electrons and d electrons, so that Sr-doped ZnO has a smaller band gap energy than pure ZnO. We would like to thank the Faculty of Mathematics and Natural Sciences for helping to facilitate research funding through the 2023 FMIPA UB Internal Fund Research.

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