Comparison of Ag and Zr substitution on the structural and optical behaviour of ZnO nanoparticles

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Abstract. Silver (Ag) and zirconium (Zr) doped ZnO (Ag-doped ZnO and Zr-doped ZnO) nanostructures were prepared utilizing the co-precipitation method, and the physical properties of all prepared samples were characterized utilizing X-ray diffractions, energy dispersive X-ray, and UV-Vis spectroscopy. Ag-doped ZnO and Zr-doped ZnO exhibit the hexagonal wurtzite structure, and the elemental analysis shows that the Ag and Zr concentrations on the samples were 3 atomic percent (at.%). The grain sizes of both samples were examined using Williamson-Hall plots with three different approaches using the uniform deformation model. The band gap energy of the prepared samples investigated using Kubelka-Munk analysis showed a red-shift to a lower energy compared to the band gap of ZnO nanoparticles, and the Zr-doped ZnO shows the lowest band gap energy. The red-shift of the band gap energy from Ag-doped ZnO and Zr-doped ZnO is probably due to the decreased grain size of both samples.

1. Introduction

Nanostructure oxide semiconductors have shown interesting physical properties, and their physical properties exhibit size dependent properties due to the quantum confinement effect. Zinc oxide is widely known as an important semiconductor material with direct band gap energy around 3.3 eV and large excitation binding energy (60 MeV) [1]. Due to several unique properties of ZnO, it has been widely used in various applications such as ultraviolet resistance, photocatalysts, photoelectric materials and energy saving materials [2].

Recently, modified ZnO with noble metals have been reported to improve the physical properties of ZnO nanoparticles. Doping ZnO with noble metal offer several advantages such as better crystallization quality and optical, electrical, and magnetic characteristics. Doping is achieved by replacing Zn\textsuperscript{2+} atoms with higher valency atoms such as Ga, Al, and In [3]. The suitability of the dopant influenced by the electronegativity and ionic radius. Therefore, it is important to determine the effective noble metal that could be doped in the ZnO crystal structure.

One of the important aspects of the noble metal is the ionic radius of the noble metal. According to several studies the Zn\textsuperscript{2+} atom has an ionic radius about 0.74 Å [4]. It is important the find the suitable dopant that has an ionic radius quite similar with Zn\textsuperscript{2+} to substitute for Zn\textsuperscript{2+} in its position [5]. This study compares the different dopant materials. In particular, Zr (Zirconium), with an ionic radius about 0.84 Å, is compared with Ag (silver), with an ionic radius about 1.12 Å [6,7].

2. Experimental details

The following starting materials that were used without further treatment are: zinc (II) sulfate (ZnSO\textsubscript{4}.7H\textsubscript{2}O, 99%, Merck) and silver sulfate [Ag(SO\textsubscript{4}), 99%, Merck], Zirconium Chloride (ZrCl\textsubscript{4}, 99%, Merck). ZnSO\textsubscript{4}.7H\textsubscript{2}O was mixed in distilled water into separate Ag(SO\textsubscript{4}), and ZrCl\textsubscript{4} solutions, and these solutions were named as solutions A and B, respectively. Both the solutions were subjected
to ultrasonic cleaning operating at 57 kHz for 2 h. Solution C was prepared by mixing 44 mmol of NaOH and 440 mL of de-ionized water. After the ultrasonic treatment, solutions A and B were placed on a magnetic stirrer at room temperature, and solution C was added to both A and B solutions until a pH of 12 was reached. The solutions were continuously mixed with a magnetic stirrer for 0.5 h, and then left undisturbed at room temperature for 18 h. The solution was then subjected to centrifugation and cleaned various times with ethyl alcohol and distilled water to purify it from residual and unwanted impurities. The precipitate was vacuum dried at 200 °C for 1 h.

The elemental analysis was characterized using energy dispersive X-ray Leo 420 in the range of 0 keV to 10 keV. The structural properties of the samples was characterized using X-ray diffraction (XRD) Philips PW 1710 with monochromatic Cu-Kα (λ = 1.54060 Å) radiation operated at 40 kV and 20 mA and 20 in the range of 10–80° was employed. Using Si powder as a standard, the instrumental broadening, including the instrumental symmetry, was calibrated. Rietveld refinement of the XRD patterns was conducted using the MAUD program to determine the crystal structure and lattice parameters. In addition, the grain sizes of the samples were calculated using Williamson-Hall plots in equation (1) for several peaks:

\[ \beta_{hkl} = \frac{\lambda\sin \theta}{D} + 4\varepsilon \sin (\theta) \tag{1} \]

where \( \beta_{hkl} \) represents the full width at half maximum (FWHM), D represents the average crystallite size, \( k \) represents the shape factor (set to 0.9), \( \lambda \) represents the wavelength of the Cu–Kα radiation, and \( \varepsilon \) represents the microstrain parameter. Optical characterizations were performed by diffuse reflectance spectroscopy, and all spectra were recorded between 250–800 nm using a Shimadzu UV-vis spectrophotometer with an integrating sphere attachment and spectral on reflectance standard. The band gap energy of the prepared samples was calculated using Kubelka-Munk analysis in equation (2):

\[ F(R) = \frac{(1 - 2R)^2}{2R} \tag{2} \]

where R represents the reflectance spectra of the samples. The energy band gap was calculated by extrapolating \( F(R) = 0 \) vs energy. Further, the thermal behaviour of the specimens was studied using differential thermal analysis (DTA) and thermogravimetric analysis (TGA) (Rigaku Thermo Plus EVO2 TG-8121). Alumina was used as the reference material and the measurements were recorded at room temperature up to 500 °C.

3. Results and discussion

The XRD spectra of Ag doped ZnO and Zr doped ZnO are plotted in figure 1. Figure 1a show that the XRD spectra of Zr doped ZnO with different doping contents have the following diffraction peaks: 2θ = 31.72°, 34.38°, 36.15°, 47.50°, 47.50°, 56.64°, 62.83°, 67.99°, and 68.88° that are attributed to the existence of the hexagonal wurtzite structure. No undesired peaks were detected that indicate the existence of a single phase of ZnO structure. The peaks intensity decreased with increased Zr doping contents probably due to the existence of Zr doping preventing the crystallization growth of the samples. However, the Ag doped ZnO exhibits different behavior than Zr doped ZnO. Figure 1b shows that the diffraction peaks of Ag doped ZnO have the same pattern at 3 at.% Ag doping content. However, increasing Ag dopant concentration to 6, 10, and 20 at.% produced the following new diffraction peaks: 2θ = 30.36°, 38.38°, and 55.27°. Thus, new peaks could be attributed to the existence of AgO samples (COD No. 1010486). It is quite interesting that the Zr doped ZnO with various dopant concentration did not produce secondary phases, while Ag doped ZnO could produce secondary phases that come from AgO. The different dopant behavior of Zr and Ag are probably due to the different ionic radii between Zr+4 and Ag+. Specifically, the Zr+4 could easily be substituted into the Zn+2 atom position in the structural of ZnO. In contrast, Ag+, with its ionic radius of 1.12 Å, which is much larger compared to Zn+2 ionic radius cannot be easily substituted into the atomic position of Zn+2 due to the limits of the solubility of Ag in the ZnO lattice.

The lattice parameters of Zr doped ZnO and Ag doped ZnO calculated using the Rietveld refinement method are presented in table 1. The table shows that the lattice parameters of Zr doped ZnO were slightly different, probably because the ionic radius of Zr+4 (0.84 Å) is larger than that of Zn+2 (0.74 Å). Increasing content of Zr causes larger lattice distortion of ZnO, which is manifested by the
Table 1. Lattice parameters, cells volume, and grain size of nanoparticles.

| Sample          | at.% | Lattice Parameters | Grain Size (nm) | Sample          | at.% | Lattice Parameters | Grain Size (nm) |
|-----------------|------|--------------------|-----------------|-----------------|------|--------------------|-----------------|
| Zr doped ZnO    | 3    | 3.2478             | 5.2069          | 23              | 3    | 3.2439             | 5.2060          |
|                  | 6    | 3.2434             | 5.1991          | 20              | 6    | 3.2471             | 5.2099          |
|                  | 10   | 3.2433             | 5.2015          | 19              | 10   | 3.2437             | 5.2068          |
|                  | 20   | 3.2461             | 5.2039          | 18              | 20   | 3.2428             | 5.2024          |
| Ag doped ZnO    | 3    | 3.2439             | 5.2060          | 26              |      |                    |                 |

Figure 1. XRD spectra of (a) Zr doped ZnO and (b) Ag doped ZnO.

measured increase in the lattice expansion. These results show the successful replacement of Zr atoms in the ZnO lattices instead of forming other lattices. The lattice parameters of Ag doped ZnO was also different with the increased Ag dopant content. This is probably because some Ag ions could substitute for the Zn ions in the ZnO lattices. The grain sizes of the samples were calculated using W-H plots as shown in figure 2. The figure reveals that the W-H plot results well fitted with the experimental data, and the grain size for both Ag and Zr doped ZnO are presented in table 1. The figure also shows that the grain size of Zr doped ZnO decreased from 23 to 19 nm, while the Ag doped ZnO decreased from 21 to 15 nm. The decreasing of band gap energy is due to the existence of a dopant that can prevent the crystal growth of ZnO nanoparticles.

The thermogravimetric analysis was investigated to understand the thermal behaviour of the prepared compositions, and the DTA/TGA of Zr and Ag doped ZnO are shown in figure 3. The thermogravimetric analysis of Zr doped ZnO shows the gradual weight lost from room temperature until 200 °C, and which 10 % can be attributed to the evaporation of water molecules in the samples (figure 3a). A difference result was observed for the Ag doped ZnO nanoparticles. The figure shows that the specimens has good stability until 350 °C (figure 3b). However, after 350 °C, the significant weight lost around 6 % followed by an exothermic process with energy x J that can be attributed to the change in phase from Ag2O to Ag nanoparticles. The DTA/TGA results from Ag doped ZnO confirm the presence of Ag2O nanoparticles in the Ag doped ZnO compositions [8].

The UV-Vis diffuse reflectance spectra of Zr doped ZnO and Ag doped ZnO are presented in figure 4. The figure reveals that the UV-Vis diffuse reflectance spectroscopy of Zr doped ZnO with different dopant concentrations have strong reflectance ability in the visible light region (400–800 nm) but no reflectance ability in the UV light region (200–400 nm). This indicates that the Zr doped ZnO possess good adsorption ability in the UV light region. The increased Zr dopant content reduces the reflectance...
Figure 2. W-H plot analysis.

Figure 3. TGA analysis of (a) Zr doped ZnO and (b) Ag doped ZnO.

ability of ZnO, indicating improved absorption ability in the visible light region of the samples with increased Zr dopant content. The reflectance spectra of Ag doped ZnO with different Ag content are plotted in figure 4a. The figure shows that the reflectance ability of Ag doped ZnO exhibits is lower compared to the reflectance ability of Zr doped ZnO. The reflectance ability of Ag doped ZnO increased when the Ag dopant content was increased from 3 to 6 at.%. However, after increasing the Ag dopant content from 10 to 20 at.%, the reflectance ability of the samples decreased. The increased reflectance ability of Ag doped ZnO from 3 to 6 at.% Ag dopant content is probably due to the formation of the secondary phase of Ag2O in the samples. Moreover, as the Ag2O contents in the samples increased, the reflectance ability of the samples in the visible light region decreased. To compare the Zr and Ag doped ZnO samples, the UV-Vis diffuse reflectance spectra of Ag and Zr doped ZnO are plotted in figure 4b. The figure shows that reflectance ability of Zr doped ZnO in the visible light region is significantly higher than the reflectance ability of Ag doped ZnO in the visible light region, which indicates the lower adsorption ability of the Zr doped ZnO sample in the visible light region compared to the Ag doped ZnO samples.

The band gap energy calculated using Kubelka-Munk analysis is presented in table 2. The figure shows that the band gap energy of Zr doped ZnO decreases with increased Zr dopant contents. The decreasing of band gap energy of Zr doped ZnO is probably due to the s–d and p–d interactions, narrowing the band gap [9]. The same behavior also occurred for Ag doped ZnO materials. The band gap gradually decreases with increased Ag doping concentration, and the decreased band gap energy is
Table 2. Band gap energy of Zr doped ZnO and Ag doped ZnO with different atomic weight percentages.

| Sample       | at.% | Band Gap (eV) | Sample       | at.% | Band Gap (eV) |
|--------------|------|--------------|--------------|------|--------------|
| Zr doped ZnO| 3    | 3.34761      | Ag doped ZnO| 3    | 3.34729      |
|              | 6    | 3.35376      |              | 6    | 3.35247      |
|              | 10   | 3.35193      |              | 10   | 3.35044      |
|              | 20   | 3.35285      |              | 20   | 3.35228      |

Figure 4. UV-Vis spectra of (a) Ag doped ZnO and (b) Zr doped ZnO.

probably due to the decreased energy gap, and this can be attributed to the p-type conductivity observed in the Ag-doped ZnO nanoparticles [10]. The doping of Ag in ZnO creates impurity band in the energy gap, which might be due to the p-type dominance in the material. Additionally, the reduction in width of energy gap has caused an increase in efficiency when these materials are used in optoelectronic devices.

4. Conclusions
The Ag and Zr substituted ZnO have successfully been synthesized by the co-precipitation method. The structural properties of Ag and Zr doped ZnO was modified with the incorporation of Ag and Zr atoms. The lattice parameters of the samples were slightly different after Ag and Zr incorporation probably due to the substitution of Zr and Ag atom in the structure of the ZnO nanoparticles. Furthermore, the heterostructure of Ag doped ZnO is due to the large differences between the ionic radii of Zn²⁺ and Ag⁺, preventing the solubility of Ag⁺ in the structure of ZnO. With increased Ag doping, a new structure was detected because of the existence of Ag₂O nanoparticles. The thermal analysis confirms that the Zr doped ZnO pose good thermal stability until 1000 °C. However, the measured lost in weight from Ag-doped ZnO at 350 °C is attributed to the change in phase from Ag₂O into silver nanoparticles. In addition, the band gap energies of the samples decreased with increased dopant content.

References
[1] Lang F, Sun D, Liu J, Wang H and Yan H 2016 Mater. Lett. 181 328–28
[2] Cao S, Zeng W, Long H, Gong J, Zhu Z and Chen L 2015 Mater. Lett. 161 275–77
[3] Soofivand F and Salavati-Niasari M 2017 J. Photochem. Photobiol. A: Chem 337 44–53
[4] Deng X, Zhang L, Guo J, Chen Q and Ma J 2017 Mater. Res. Bull. 90 170–4
[5] Wei H, Guo W, Sun Y, Yang X and Zhang Y 2010 Mater. Lett. 64 1424–26
[6] Zorkipli N.N.M, Noor Haida Mohd Kaus N.H.M, Mohamad A.A 2016 *Procedia Chem.* **19** 626–31
[7] Cao A, Zeng W, Li T, Gong J and Zhu Z 2015 *Mater. Lett.* **156** 25–7
[8] Suresh R, Ponnuwamy V, Sankar C, Manickam M, Venkatesan S and Perumal S 2017 *J. Magn. Magn. Mater.* **441** 787–94
[9] Rubinstein A, Kodama R.H and Makhlouf S.A. 2001 *J. Magn. Magn. Mater.* **234** 289–93
[10] Hernández A, Maya L, Sánchez-Mora E and Sánchez E M 2007 *J. Sol–Gel Sci. Technol.* **42** 71–8