Influence of doping Co to characterization of ZnO nanostructures

Minh Thuy Doan, Xuan Vinh Ho, Tu Nguyen and Van Nghia Nguyen

Faculty of Physics, Quy Nhon University, 170 An Duong Vuong, Quy Nhon, Binh Dinh, Vietnam
E-mail: doanminhthuy@qnu.edu.vn

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Abstract
Cobalt doped zinc oxide nanoparticles were successfully synthesized using the hydrothermal method. The structure of these nanoparticles studied using x-ray diffraction clearly presented the existence of Co3O4 phase in the 4% Co-doped ZnO samples. Field-emission electron scanning microscopy (FESEM) was used to examine the morphologies of products. Optical absorption measurements confirm the presence of a strong ultraviolet peak at 374 nm. The room temperature photoluminescence spectra investigated under the excitation at 325 nm by a neon laser exhibit both the ultraviolet and visible emission bands.

Keywords: nanopowder, zinc oxide, Co-doped ZnO, photoluminescence

1. Introduction
Experimental and theoretical researches on diluted magnetic semiconductors have been attracting much attention for the potential applications in various fields of science and technology as well as industry. Zinc oxide reveals the direct wide band-gap and large exciton binding energy, which leads to the possible uses in optoelectronics [1–4]. Among these materials, cobalt doped zinc oxide emerged as one of the most prospective candidates in spintronics devices due to its room temperature ferromagnetic behavior. There are many methods to synthesize Co-doped ZnO nanoparticles, such as chemical vapor deposition (CVD), laser ablation, microwave [5, 6]. We chose the hydrothermal method to synthesize the Co-doped ZnO nanoparticles from zinc acetate Zn(CH3COO)2.2H2O and cobalt chloride CoCl2.6H2O because the technique is a simple, efficient, cost-effective and convenient route for large quantities. Recently, several groups reported on Raman and photoluminescence spectra of Co-doped ZnO. The influence of the doping concentration of cobalt, however, is still under debate.

In this work the morphology, structure and optical properties of Co-doped ZnO nanostructures with different Co contents were investigated by different techniques. Those samples were characterized by x-ray diffraction (XRD) using a Siemens D5005 with Cu-Kα (λ = 1.5406 Å) radiation to identify the crystalline structure. The morphologies and microstructures were investigated using a JEOL JEM-1010 transmission electron microscope (TEM). The optical absorption spectra of the samples were carried out using a UV-Vis Cary 5000. The energy excitation of 325 nm of a neon laser was exploited to investigate the room temperature photoluminescence spectra of the samples.

2. Experimental
Co-doped ZnO nanoparticles were fabricated using zinc acetate Zn(CH3COO)2.2H2O (Merck, Germany) and cobalt chloride CoCl2.6H2O (Merck, Germany). The 0.03 mol of zinc acetate dissolves in the 20 mL of ethanol. The amount of cobalt chloride dissolves in the 10 mL of ethanol. The two above solutions were stirred magnetically for 30 min. They were mixed and stirred magnetically for 30 min to obtain the solution. Then, the 20 mL of polyvinylpyrrolidone (PVP) diluted in ethanol was poured into the mixture and stirring magnetically was continued for 3 h. The amount of sodium hydroxide dissolved in the 40 mL of ethanol was added drop by drop into the above mixture and stirred for 8 h. After that, the mixture was put into the Teflon container and hydrolyzed.
3. Results and discussion

3.1. Structural study

Figure 1 showed the XRD spectra of Co-doped ZnO samples with Co content at 0, 1, 2, 3 and 4% investigated using Siemens D5000 with Cu-Kα radiation with the wavelength of 1.54 nm. The peaks at scattering angles (2θ) of 32°, 34.5° and 36.5° corresponding to the reflection from (100), (002) and (101) crystal planes, respectively, are observed. XRD patterns show that the intensity of peaks is strong and the width of peaks is narrow, which indicate that samples possessed uniform nature of the crystallites. There are no shifts of the peaks among the samples.

The spacing \(d\) of the \((hkl)\) set of lattice plane in wurtzite crystal structure depends on lattice constants and Miller indices of lattice plane \((hkl)\) as follows

\[
\frac{1}{d^2} = \frac{4}{a^2} \left( \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right).
\]

The lattice parameters \(a\), \(c\) change a little randomly (table 1). Our results agree with those of Yang’s group [4]. The group of Chang [7], however, indicated that the lattice parameter \(a\) expands slightly with the increase of Co content while the lattice parameter \(c\) remains unchanged. These different results between two groups may result from the following reason: the radius of Co\(^{2+}\) ion (0.58 Å) is close to that of Zn\(^{2+}\) ion (0.60 Å).

XRD patterns of the 4% Co-doped ZnO samples indicated the appearance of a peak that corresponds to Co\(_2\)O\(_4\) phase beside the peaks related to the wurtzite phase and the width of the peaks was also expanded. These changes may originate from the substitution of Co\(^{2+}\) ions for Zn\(^{2+}\) ions. Furthermore, Co\(^{2+}\) ions that do not replace the lattice position of Zn\(^{2+}\) ions generate the Co\(_2\)O\(_4\) phase. From the XRD result it can be deduced that the wurtzite crystal structure still remains unchanged, but the quality decreases.

3.2. Morphological study

The morphologies of Co-doped ZnO samples doped with different Co contents were examined using a field-emission electron scanning microscope (FESEM) Hitachi S4800 (figure 2). Figure 2(A) shows that pure ZnO nanostructures were nanosheets with thickness of about 40–50 nm. The Co-doped ZnO samples with the Co content ranging from 0% to 3% (figures 2(A)–(D)) exhibited particle shape with a clear border, while the 4% Co-doped ZnO samples exhibited rod-like shape with surface defects (figure 2(E)).

3.3. Optical properties

Figure 3 shows the UV-Vis spectrum of the Co-doped ZnO samples with different Co contents. The optical absorption coefficient \(\alpha\) of direct semiconductor nanomaterials at energies close to the band edge can be expressed by the following formula

\[
\alpha = A \left( \frac{h\nu - E_g}{h\nu} \right)^{1/2},
\]

where \(\alpha\) is the absorption coefficient, \(E_g\) is the absorption band gap, \(A\) is constant [8]. The curves of \((\alpha h\nu)^2\) versus \((h\nu)\) can be obtained based on the absorption data in the inset in figure 3. From figure 3, the values of 3.43, 3.20 and 3.10 eV are supposed to be the energy gap of ZnO, 2% Co-doped ZnO and 4% Co-doped ZnO samples, respectively. It can be seen obviously that the band gaps of Co-doped ZnO samples decrease with the increase of the Co level. According to Udayakumar et al as the doping concentration is increased, electrons populate states within the conduction band which pushes the Fermi level toward higher energy leading to the expansion of energy gap [9]. The effect is known as Burstein–Moss effect. In contrast, Yang’s group pointed out that the defects in the crystal cause the red-shift of energy gap [4]. We believe that the changes of band gap depend on both Burstein–Moss effect and defects in the crystal.

Under 325 nm line excitation of a neon laser, the room temperature photoluminescence (PL) of the Co-doped ZnO samples with the Co content ranging from 0% to 4% presents two emission regions: ultraviolet and visible regions. In the visible region, the PL intensity of Co-doped ZnO samples decreases with the concentration of Co increasing from 0% to 3% due to the substitution of Co\(^{2+}\) ions for Zn\(^{2+}\) ions, whereas that of 4% Co-doped ZnO sample is considerably enhanced in comparison to the pure ZnO sample (figure 4).
Figure 2. The SEM images of Co-doped ZnO samples with different Co contents. (A) 0%, (B) 1%, (C) 2%, (D) 3% and (E) 4% Co-doped ZnO.

Figure 3. The curves of \((\alpha h \nu)^2\) versus \((h \nu)\) of the Co-doped ZnO samples with different Co contents.

Figure 4. PL spectra of the Co-doped ZnO samples with different Co contents.

Table 1. The lattice parameters of Co-doped ZnO samples with different Co contents.

| hkl   | 100     | 002     | 101     |
|-------|---------|---------|---------|
|       | \(d\) (Å) | \(a\) (Å) | \(c\) (Å) | \(d\) (Å) | \(a\) (Å) | \(c\) (Å) | \(d\) (Å) | \(a\) (Å) | \(c\) (Å) |
| ZnO   | 2.9787  | 3.2118  | 5.5974  | 2.5880  | 2.9884  | 5.1761  | 2.4664  | 2.8479  | 4.9327   |
| ZnO-Co 1% | 2.8050  | 3.2389  | 5.6100  | 2.5960  | 2.9976  | 5.1920  | 2.4890  | 2.8740  | 4.9780   |
| ZnO-Co 2% | 2.8000  | 3.2332  | 5.6000  | 2.5940  | 2.9953  | 5.1880  | 2.4680  | 2.8498  | 4.9360   |
| ZnO-Co 3% | 2.8000  | 3.2332  | 5.6000  | 2.5910  | 2.9918  | 5.1820  | 2.4680  | 2.8706  | 4.9720   |
| ZnO-Co 4% | 2.8061  | 3.2402  | 5.6122  | 2.5943  | 2.9957  | 5.1886  | 2.4620  | 2.8429  | 4.9240   |
introduction of Co$_3$O$_4$ phase in the 4% Co-doped ZnO samples leads to the enhancement of the PL intensity. Moreover, the strong visible emission peaks at around 610 nm exhibit the red-shift phenomena. Besides, the ultraviolet emission band of the Co-doped ZnO samples is expanded compared to that of pure ZnO. The most widely accepted origin of this kind of emission is properly due to the introduction of defects by the doping of Co and the presence of $-\text{OH}$ group, which results in the increase of the recombination processes of electrons in conduction band with holes in valence band as well as the band-edge excitation of ZnO.

4. Conclusion

Co-doped ZnO nanostructures were successfully fabricated using the hydrothermal method. When the cobalt doping concentration increases from 0 to 4%, the morphologies of products transfer from nanosheets to nanoparticles and to nanorods, but the lattice structure was unchanged. In the PL spectra, the peak’s position of the visible emission shifts to long wavelength with the increase of Co content. The Co$_3$O$_4$ phase clearly presents in the Co-doped ZnO sample at the cobalt level of 4%, which causes the strong PL in the visible region compared to the other samples.

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