Synthesis of undoped and M-doped ZnO (M = Co, Mn) nanopowder in water using microwave irradiation

Nguyen Viet Tuyen¹, Ta Dinh Canh¹, Nguyen Ngoc Long¹, Nguyen Xuan Nghia², Bui Nguyen Quoc Trinh³ and Zhongrong Shen³

¹ Faculty of Physics, College of Science, Vietnam National University, Hanoi
² Institute of Materials Science – VAST
³ Shimoda Nano-Liquid Process Project, ERATO, Japan Science and Technology Agency (JST) 2-5-3 Asahidai, Nomi, Ishikawa 923-1211

Abstract. Undoped and M-doped ZnO (M = Co, Mn) nanopowders have been successfully synthesized by microwave-assisted approach using Zn(NO₃)₂.2H₂O and NaOH. The results obtained from X-ray diffraction (XRD) analysis and the transmission electron microscopy (TEM) showed that the mean particle size was about 10-15 nm. The XRD analysis of the synthesized samples also showed a single phase ZnO structure without any additional phase. Magnetic property studies of the as-prepared M-doped ZnO (M = Co, Mn) samples showed them to be paramagnetic material. However, thermal annealing in air of particular samples at 800°C for 3 h resulted in transforming the samples into a room temperature ferromagnetic material.

Keyword: Nanopowder, undoped and M-doped ZnO (M = Co, Mn), microwave irradiation.

1. Introduction
Zinc oxide (ZnO) nanoparticles are used in a variety of applications such as ultraviolet (UV) light emitting device [1], catalyst [2], photo-catalyst [3], electro-acoustic wave device, and UV detector [4].

ZnO technologically is an important material due to its wide range of optical and electrical properties as well as semiconductor crystal with a large exciton binding energy (60 meV) and wide band gap (3.37 eV). The stable structure of ZnO is wurtzite, in which four atoms of oxygen locate in tetrahedral coordination surround each atom of zinc. Recently, Co-, Mn-doped ZnO have been investigated for possible application as spintronic material [6]. Synthesis of these materials is often accomplished by sputtering [7], chemical vapor deposition [8] and sol-gel technique [9, 10].

In this paper, we report a simple method for preparation of hexagonal undoped and M-doped (M = Co, Mn) by using microwave irradiation. Microwave-solvothermal synthesis is generally faster, more simply and energy efficient.

2. Experimental
The ZnO nanopowders were synthesized under the microwave irradiation in a tube water cooling systems (figure 1). The ZnO nanopowders were prepared according to the following equations:

\[
\text{Zn(NO}_3\text{)}_2 + \text{NaOH} \rightarrow \text{Zn(NO}_3\text{)}_2\text{(OH)} + \text{NaNO}_3
\]

(1)

\[
\text{Zn(NO}_3\text{)}_2\text{OH} + \text{NaOH} \rightarrow \text{ZnO} + \text{NaNO}_3 + \text{H}_2\text{O}
\]

(2)
and the NaNO₃ was removed by washing the sample with water.

Figure 1. Image of microwave irradiation system.

Synthesis of ZnO nanopowders was achieved by dissolving 1.89 g zinc nitrate (Merk, 99% purity) in ethanol to make a 50 ml solution of 0.2 M Zn(NO₃)₂ (Merk, 99% purity). While stirring, 50 ml of 0.4 M NaOH (Merk, 99% purity) was added dropwise. The resulting solution (the final pH of the solution was 12) was then placed in a conventional microwave. The microwave power was set to 150 W and the reaction time was 5 minutes. During the microwave irradiation the temperature of the solution reached up 80°C. After 5 minutes, a white product precipitated, the precipitator was washed several times with absolute ethanol and distilled water. This process was repeated until the pH of the solution was 7. Finally, the product was dried at 70°C for 4 hours. For doping, appropriate amounts of metal nitrates such as Co(NO₃)₂, Mn(NO₃)₂ (Merk, 99% purity) were added to zinc nitrate solution until the concentration of the dopant was 5%.

The particle morphologies and structures of the products were investigated by a transition electron microscope (TEM JEM 1010-JEOL), high-resolution transmission electron microscope (HRTEM JEM 2010-JEOL) and X-ray diffractometer (Bruker-AXS D5005). Raman scattering spectra at room temperature in the energy region between 100 and 1000 cm⁻¹ were recorded by a micro-Raman spectrograph LABRAM-1B equipped with a He-Ne laser (λ = 632.8 nm) with a power of 11 mW. Photoluminescence (PL) measurement at room temperature was carried out on a 325 nm He-Cd laser.

3. Results and discussion
X-ray diffraction is used to investigate the changes of phase structure and crystallite size of the undoped ZnO powders and the 5% transition metal-doped ZnO samples. Figure 2 shows the XRD patterns of the undoped ZnO samples and Co- and Mn-doped ZnO samples, which demonstrates that all the ZnO samples have wurtzite hexagonal structure [4]. As indexed in the figure, all the diffraction peaks match those of wurtzite ZnO with lattice constants of a = 3.250 Å and c = 5.207 Å. The strong diffraction peaks appear at 31.8, 34.3 and 36.5°, which correspond to (100), (002) and (101) planes of wurtzite ZnO, respectively. The average crystallite size of the samples, evaluated by the Scherrer formula [5], is about 13 nm. This value agreed well with TEM observations of the ZnO nanopowders. It should be pointed that in the XRD patterns except the diffraction peaks of ZnO, no peak of additional phase was observed.
Further, Raman scattering, due to its sensitivity to the crystallization, structural disorders and defects in nanostructures, was measured for the ZnO nanoparticles. Figure 3 shows the Raman spectrum of ZnO nanoparticles. ZnO has a wurtzite crystal structure and belongs to C\textsubscript{6v} group. According to group theory analysis, the A\textsubscript{1}+E\textsubscript{1}+2E\textsubscript{2} modes are Raman active. The two higher peaks at 103 and 438 cm\textsuperscript{-1} can be assigned to E\textsubscript{2} modes, characteristic of the wurtzite lattice. The much weaker peak at 379 cm\textsuperscript{-1} is attributed to the transverse optical modes of A\textsubscript{1}. The other two weaker and broader peaks at 203 and 333 cm\textsuperscript{-1} can be assigned to the secondary Raman scattering arising from zero-boundary phonons 2-TA (M) and 2-E\textsubscript{2} (M), respectively [8]. The presence of the E\textsubscript{1} (LO, 580 cm\textsuperscript{-1}) mode of oxygen deficiency indicates that there are oxygen vacancies in our ZnO nanoparticles.

The EDS elemental analysis is shown in figure 4. This result indicates that ZnO nanoparticles were only composed of Zn and O. This suggested a high purity of the ZnO nanopowder.

TEM is used to observe the particle size and morphology of the samples. Figure 5 shows the TEM photographs of the undoped and the 5% transition metal-doped ZnO samples.
Figure 5. TEM images of the undoped and doped ZnO nanoparticles: a) ZnO; b) Co-doped ZnO; c) Mn-doped ZnO, prepared with the microwave power of 150 W.

In figure 6 the morphology of the ZnO nanoparticles prepared with different powers of the microwave is presented. It can be seen that decreasing power of the microwave results in an aggregation of the nanoparticles.

The morphology and structure of powders were further investigated by TEM. TEM gives us more details about microstructure of the ZnO nanopowders, as shown in figure 7. The nanopowders are of good transparency to the electron beam. The particles appeared to be well separated from each other. Figure 7a shows the morphologies of ZnO nanoparticles containing mainly spherical particles typically with diameters ranging from 10-15 nm. The micrographs revealed that the particles were nearly spherical in shape (figure 7b). Figure 7c shows an electron diffraction (ED) pattern of the produced nanopowder. The ED pattern shows ring patterns without any additional spots and rings of secondary phases revealing their highly crystalline ZnO wurtzite structure. Three fringe patterns were observed with plane distances of 2.79, 2.58, and 2.44 Å in the electron diffraction pattern which corresponds to (100), (002), and (101) planes of pure wurtzite hexagonal structure of ZnO. The fringe spacing is about 0.28 nm, corresponding to the (100) crystal planes of ZnO (figure 7d). The ED patterns illustrate crystalline, which is in good agreement with the XRD data. The ZnO nanoparticles can be observed as particles having the hexagonal and spherical shapes.

Photoluminescence and absorption spectra of the undoped and Co- and Mn- doped ZnO nanoparticles are shown in figure 8 and figure 9, respectively.
Figure 7. (a) TEM image of ZnO nanopowder; (b) magnified TEM image of ZnO nanopowder; (c) corresponding electron diffraction pattern, and (d) HRTEM image of single ZnO nanoparticle showed (100) crystalline planes.

The absorption spectrum of ZnO nanoparticles dispersed in ethanol solution is shown in figure 8. Compared with bulk ZnO, the blue shift observed in the ZnO nanostructures is due to the quantum size effect.

The green emission band is attributed to the radiative recombination of photogenerated holes with electrons belonging to singly ionized oxygen vacancies on the surface and subsurface. The observation of strong green band emission relative to bulk ZnO indicates the existence of oxygen vacancies concentrated on nanoparticles surface.

Figure 8. The PL spectrum of undoped ZnO nanopowder. The inset shows UV-vis spectrum of the ZnO nanopowder.

Figure 9. The PL spectrum of the 5% Co- and 5% Mn-doped ZnO samples annealed at 800°C in air for 3 hours. The inset shows UV-vis spectra of Co- and Mn-doped ZnO nanopowder.
The PL spectra of the 5% Co- and 5% Mn-doped ZnO samples annealed at 800°C in air for 3 h (figure 9) are similar to that of undoped ZnO nanopowder. However, besides the broad band at 591 nm, it is noted that there is another peak at 682 nm with a full width at half maximum of 110 meV, which is attributed to the 3d-3d electron transitions. The authors [11, 12] assert that this radiation band corresponding to the $^4T_1 \rightarrow ^4A_2$ transition of Co$^{2+}$ or Mn$^{2+}$ in the crystalline network ZnO.

The as-prepared samples of 5% Co-doped ZnO and 5% Mn-doped ZnO display a paramagnetic behavior, but after annealing at 800°C in air for 3 h, these samples display room temperature ferromagnetism as can be seen from the hysteresis loop shown in figure 10.

The remanence ($M_r$) and coercive field ($H_c$) data for the annealing in air samples displaying ferromagnetism are $M_r = 0.35 \times 10^{-4}$ emu/g, $H_c = 88$ Oe for Co-doped ZnO samples and $M_r = 0.29 \times 10^{-4}$ emu/g, $H_c = 29$ Oe for Mn-doped ZnO samples, respectively. So we strongly believe that when ZnO crystallites were doped with cobalt or manganese, Co$^{2+}$ ions or Mn$^{2+}$ ions substituted for Zn$^{2+}$ ions.

**Figure 10.** Magnetization as a function of magnetic field for a) 5% Mn-ZnO samples annealed at 800°C in air for 3 hours; b) 5% Co-ZnO samples annealed at 800°C in air for 3 hours; and c) as-prepared samples.

### 4. Conclusion

The easy and very fast microwave-assisted approach was used for preparation of the undoped and M-doped ZnO (M = Co, Mn) nanoparticles. The XRD measurements showed the formation of single phase compound without any additional phase and the magnetic measurements showed that the as-prepared cobalt- or manganese-doped zinc oxide is paramagnetic. However, thermal annealing of these samples at 800°C in air for 3 hours transforms the magnetic nature from paramagnetic to ferromagnetic. The particle sizes of 10-15 nm determined by using Scherer formula were in good agreement with TEM observations. This microwave-assisted technique may possibly be extended for synthesis of other transition metal-doped oxides.

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Acknowledgments

This work is supported by the Fundamental Research Program, Ministry of Science and Technology of Vietnam (Project No 405506) and by Vietnam National University, Hanoi (Project QG 09 05).