Research Article

Wet Chemical Preparation of Nanoparticles ZnO:Eu^{3+} and ZnO:Tb^{3+} with Enhanced Photoluminescence

Tran Kim Anh,^{1,2,3} Dinh Xuan Loc,¹ Nguyen Tu,^{3,4} Pham Thanh Huy,³
Le Minh Anh Tu,¹ and Le Quoc Minh^{1,2}

¹ Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam

² Duy Tan University, 182 Nguyen Van Linh, Da Nang, Vietnam

³ Advanced Institute of Science and Technology, HUT, 1 Dai Co Viet, Hanoi, Vietnam

⁴ Department of Physics, Quy Nhon University, Vietnam

Correspondence should be addressed to Le Quoc Minh; lequocminhvn@gmail.com

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ZnO doped with Eu^{3+} and Tb^{3+} had been successfully prepared by wet chemical method with the assistance of microwave. The influence of reaction conditions such as temperature, time, content of Eu^{3+} , Tb^{3+} ion, and annealing treatment on the structure and luminescent characteristics was studied. The analysis of energy dispersive spectroscopy (EDS) and photoluminescence spectra measurements indicated that Eu^{3+} and Tb^{3+} exist in host lattice and create the new emission region compared to ZnO crystalline host lattice. The field emission scanning electron microscope (FE-SEM) studies show the Eu^{3+} , Tb^{3+} doped ZnO nanoparticles have a pseudohexagonal shape. The particle size was 30–50 nm for ZnO:Eu^{3+} and 40–60 nm for ZnO:Tb^{3+} . Photoluminescence excitation (PLE) and photoluminescence (PL) spectra at room temperature have been studied to recognize active centers for characteristic luminescence of ZnO:Eu^{3+} and ZnO:Tb^{3+} . The characteristic luminescent lines of Eu^{3+} (${}^5\text{D}_0$ – ${}^7\text{F}_j$) and Tb^{3+} (${}^5\text{D}_4$ – ${}^7\text{F}_j$) were determined. It has been demonstrated that the wet chemical synthesis method with microwave assistance can strongly enhance the luminescent intensity of nanoparticles ZnO:Eu^{3+} in red and ZnO:Tb^{3+} in green.

1. Introduction

Rare earth (RE) doped ZnO has been increasingly taking an important role in optoelectronics and photonics [1, 2]. In several industrial branches such as ceramics, rubber additives, pigments, and medicines, ZnO has been widely used. ZnO represents as a wide-band gap semiconductor ($E_g = 3.37$ eV at 300 K) with a large exciton binding energy (60 meV), exhibiting near UV emission and piezoelectricity with high optical gain. ZnO is also biosafe and biocompatible and may be used for biomedical applications. Recently, the discovery of the ultraviolet laser and piezoelectric and photocatalysis properties of ZnO nanostructures has triggered several new applications. Various physical and chemical routes, such as physical vapor deposition, thermal evaporation, chemical vapor deposition (CVD), metal-organic chemical vapor deposition, and colloidal wetting chemical synthesis, have been used to prepare a wide range of ZnO nanostructures

[3–12]. These superior properties of ZnO make it suitable for short-wavelength optoelectronic devices application such as light emitting diodes, laser diodes, and room-temperature UV laser diodes [13]. Furthermore, ZnO:RE nanoparticles, nanorods, nanowires, nanobelts, and thin films with their unique structure properties and physical properties have been widely fabricated in using the different wet chemical solution methods [14–20].

In this work, we present new results of fabrication, morphology, and emission properties of ZnO:Eu^{3+} and ZnO:Tb^{3+} nanoparticles prepared by wet chemical method with assistance of microwave (MW) heating.

2. Experimental

The samples were prepared by wet chemical synthesis with MW assistance. All reagents $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, NaOH,

$\text{CO}(\text{NH}_2)_2$, EuCl_3 , and TbCl_3 were in analytic purity grade and purchased from Aldrich. Deionized water was used as dispersing agent. A commercial microwave reactor system MASII (Sinco Co) has been used for the fabrication of $\text{ZnO}:\text{Eu}^{3+}$, $\text{ZnO}:\text{Tb}^{3+}$ nanomaterials. This MASII reactor could control automatically microwave power, temperature, and time of reaction. The typical fabrication conditions were of microwave power 500 W, at temperatures 40°C, 60°C, and 80°C. The exposure time of MW was 30 minutes. The doping contents of Eu^{3+} and Tb^{3+} ions in ZnO host materials were about 5% mole [5]. For the preparation of Eu^{3+} and Tb^{3+} ions doped ZnO sample, 60 mL of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CO}(\text{NH}_2)_2$ solution (0.05 M) was added 1 mL EuCl_3 (TbCl_3) solution (0.15 M). Then the resulting solution was stirred constantly for 10 min. Then the resulting solution was poured in the reaction holder of MASII reactor. After the completion of MW exposure, the reaction solution cooled down to room temperature. The fabricate was collected by centrifugation with speed 5000 rpm, washed with deionized water and ethanol, and filtered to the ultimate white product, which was dried in vacuum for 20 h at 60°C to get the ZnO doped with Eu^{3+} and Tb^{3+} ions fine powder. The annealing treatment of $\text{ZnO}:\text{Eu}^{3+}$, $\text{ZnO}:\text{Tb}^{3+}$ samples was at 900°C for 2 h in Ar gas atmosphere.

A field scanning electron microscope FE-SEM with EDX (JEOL7600F) has been used for surface morphology and compositional analysis of the prepared ZnO samples. The photoluminescence (PL) emission and photoluminescence excitation (PLE) studies were carried out by commercial Nanolog iHR 320 spectrophotometer with 150 W xenon lamp or He-Cd laser IK5525R-F (KIMMON Inc) with wavelength of 325 nm as excitation source, in wavelength range 350 nm–750 nm.

3. Results and Discussion

The particle morphology of Eu^{3+} and Tb^{3+} doped ZnO samples were shown in the FE-SEM images. Figure 1 shows the FE-SEM image of $\text{ZnO}:\text{Eu}^{3+}$ sample, which is prepared at temperature 80°C and microwave power 500 W and for 30 minutes. As can be seen, the whole sample is nearly hexagonal in shape with size about 30–50 nm. Besides, the size of $\text{ZnO}:\text{Eu}^{3+}$ nanoparticles is about 40–60 nm. It is also observed that the surface of the prepared sample is smooth and uniform with no cracks on it.

For compositional analysis by using the EDX method, it needs to sputter a Pt metal thin layer on the surface of sample due to the high emission property of RE (Eu^{3+} , Tb^{3+}) doped ZnO nanomaterials. In Figure 2, the EDS signals of elements of Zn, O, Eu, and also Pt can be seen. Based on the analyses of EDX spectra, it can be obtained the elemental contents of Zinc 29.19%; Europium 1.97% and Oxygen 65.42% in atomic rate and also 48.63%; 7.63% and 26.67% on weight, respectively. It shown in Table 1. It can be concluded that the Eu doping in ZnO matrix has been successfully implemented by using the wet chemical synthesis method in microwave assistance.

FIGURE 1: FE-SEM image of $\text{ZnO}:\text{Eu}^{3+}$ nanoluminophor sample grown at 80°C for 30 minutes by microwave system 500 W.

Full scale 296 cts cursor: 0.000

FIGURE 2: EDS spectrum of $\text{ZnO}:\text{Eu}^{3+}$ 5% nanopowder.

TABLE 1: Weight % and atomic % of $\text{ZnO}:\text{Eu}^{3+}$ 5% nanopowder.

Element	Weight %	Atomic %
O K	26.67	65.41
Zn K	48.63	29.19
Eu L	7.63	1.97
Pt M	17.07	3.43
Total	100.00	100.00

The room temperature photoluminescence emission and excitation spectra of the $\text{ZnO}:\text{Eu}^{3+}$ samples are shown in Figures 3 and 4. The emission spectra taken at emission wavelength $\lambda_{\text{ex}} = 394$ nm for $\text{ZnO}:\text{Eu}^{3+}$ shown the main emission peaks at 590 nm, 615 nm, 652 nm, and 695 nm (Figure 4). These luminescence lines can be assigned to the f-f transitions of Eu^{3+} ions: ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$, ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$, and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$, respectively. Among them, the emission characteristic of Eu^{3+} , in which the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition at 615 nm is the most prominent emission peak, which results the emission in red color of ZnO nanoparticles doped with Eu^{3+} . Photoluminescence excitation spectra of $\text{ZnO}:\text{Eu}^{3+}$ samples taken at monitoring wavelength at 615 nm shown that the peaks at 394 nm, 415 nm, 464 nm, and 534 nm correspond to the transitions ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_3$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$, and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$, respectively. Among them, there are two prominent peaks at 394 nm and

FIGURE 3: Photoluminescent excitation of ZnO:Eu^{3+} , monitored at emission line 615 nm.

FIGURE 4: Photoluminescent spectrum of ZnO:Eu^{3+} 5% excited by 394 nm.

464 nm (Figure 3). A peak at 357 nm is quite prominent may be due to the host to guest charge transfer and f-f transitions, respectively.

Based on the PLE and PL spectra analysis, an energy transfer process from ZnO host nanomaterials to RE (Eu , Tb) ions may be proposed. Generally, two different excitation mechanisms could be proposed for Ln^{3+} (Eu^{3+} , Tb^{3+}) ions in ZnO matrix, first a direct excitation into high energy multiples of 4f level of Ln^{3+} and second via the defect-related band of ZnO lattice. It shown in Figure 3, the PLE spectra of ZnO:Eu^{3+} sample consist of several peaks having two characteristic one at 394 nm and 464 nm, when the emission wavelength at 543 nm was as monitor. These bands were overlapped intense and sharp emission centered at about 387 nm and the other broad band at about 554 nm [18]. In

FIGURE 5: Photoluminescent spectra of ZnO:Eu^{3+} 5% prepared at 40°C (red), 60°C (green) and 80°C (black).

FIGURE 6: Photoluminescent spectra of ZnO:Eu^{3+} 5% as prepared (black) and annealing at 900°C (red).

Figure 4, when excitation was made at 394 nm, the PL spectra shown several characteristic emission lines, which is from the transitions between its intra-4f electron energy level that correspond to $^5\text{D}_0 \rightarrow ^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$). In short, since the defect state energy of the ZnO lattice is close to the photon energy, it provided excitation of the $^7\text{F}_0 \rightarrow ^5\text{D}_2$ of Eu^{3+} ions. The electrons then transfer from the $^5\text{D}_0$ state to the $^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$) of Eu^{3+} ions, resulting in a red luminescence [21]. In the case of ZnO:Tb^{3+} the energy transfer from ZnO host lattice to the photon energy levels

FIGURE 7: Photoluminescent excitation of ZnO:Tb³⁺ 5% monitored at 542 nm (a) and photoluminescent spectrum of ZnO:Tb³⁺ 5%, excitation at 374 nm (b).

of Tb³⁺ ions occurred. it excited the $^7F_5 \rightarrow ^5D_4$ transition of Tb³⁺ ions, which is creating a green luminescence [15].

The luminescent spectra of ZnO:Eu³⁺ samples prepared at temperatures 40°C, 60°C, and 80°C are shown in Figure 5. It could be seen that when the synthesis temperature increased, the luminescent intensity of Eu³⁺ much strongly increased. When the reaction carried out at temperature 40°C, the emission from Eu³⁺ could be hardly seen. At reaction temperature 60°C, the emission intensity of Eu³⁺ was comparable to that of ZnO host material. When the reaction temperature increased up to 80°C, the emission became mostly from Eu³⁺. Figure 6 shows the photoluminescent spectra of ZnO:Eu³⁺ 5% as prepared and annealing at 900°C in Ar. It is noted that the luminescence intensity of ZnO:Eu³⁺ sample after the 900°C annealing was twofold stronger than that of the as prepared one. It indicates that the annealing has played a great role in the luminescence intensity of ZnO:Eu³⁺ nanomaterials.

Figure 7 shows the PLE and PL spectra of ZnO:5%Tb³⁺ prepared at 80°C. All characteristic transitions of Tb³⁺ ion at 490 nm, 543 nm, 590 nm, and 621 nm were observed, when excited by 374 nm. The luminescent intensity of ZnO:5%Tb prepared at 80°C was stronger than that of at 60°C and 40°C. Furthermore, the PL spectra show four significant peaks between 450 nm and 650 nm, which are corresponding to the $^5D_4 \rightarrow ^7F_j$ transitions of Tb³⁺ ions: $^5D_4 \rightarrow ^7F_6$ (490 nm), $^5D_4 \rightarrow ^7F_5$ (543 nm), $^5D_4 \rightarrow ^7F_4$ (590 nm), and $^5D_4 \rightarrow ^7F_3$ (621 nm). The transition $^5D_4 \rightarrow ^7F_5$ for 543 nm was the highest intensity.

4. Conclusion

In summary, Eu³⁺ and Tb³⁺ doped ZnO nanomaterials have been successfully synthesized at low temperature and short reaction time by wet chemical method with microwave assistance. The reaction temperature and annealing treatment have great influence on luminescent intensity of the ZnO:Eu³⁺ and ZnO:Tb³⁺ nanoparticles. The nanoparticles ZnO:5%Eu³⁺ with 30–50 nm and ZnO:5%Tb³⁺ with 40–60 nm have been prepared. The PLE and PL spectra have been investigated. Energy transfer takes place effectively from ZnO host matrix to RE (Eu³⁺, Tb³⁺) ions, which results in high luminescence of Eu³⁺ in red and of Tb³⁺ in green color. These ZnO:Eu, Tb nanoluminophors materials could be used in many applications' fields such as optoelectronic, display, lighting, and security printing.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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