Effects of the Cu Ion on the Structural and Optical Properties of Yttrium Doped ZnO by Solution Combustion

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Abstract

In this experiment, pure, Y³⁺ doped ZnO and Cu²⁺ + Y³⁺ co-doped ZnO were synthesized by a solution combustion method. The Y³⁺ dopant concentration was fixed in 3%wt. and the Cu²⁺ dopant concentrations were 0, 1, 2, 3, 10, and 20%wt. The XRD spectra showed that the original hexagonal wurtzite structure of ZnO is conserved after doping process, an increasing red shift until 10%wt. Cu²⁺ doping and decrease at higher Cu²⁺ doping and also, the chemical creation of the new Y₂O₃ and Y₂Cu₂O₅ phases. The behavior of the photoluminescence of the samples as a function of Cu²⁺ doping reveal that the green emission band of the ZnO is quenching and the ZnO UV emission intensity decrease notably for all Cu²⁺ doping. The scanning electron microscope analysis of the Cu²⁺ + Y³⁺ co-doped ZnO samples reveal the existence of grains agglutinated forming like-spheres particles. However, the nano-sized characteristic of the crystals is confirmed.

Keywords

Zinc Oxide, Solution Combustion, X-Ray, Photoluminescence, Morphology

1. Introduction

The zinc oxide (ZnO) is one of the oldest n-type semiconductor material studied, and is actually a promising material in fundamental studies and technological applications due to its varied and outstanding properties such as: high conductance and transparency in thin films, chemical and thermal stability, wide band gap (3.37 eV) and a large exciton binding energy (60 meV) [1], which presents efficient photoluminescence and thermo-luminescence in intrinsic state.
The property that has the ZnO of can be doped opened a lot of technological applications: doping of ZnO for fabricating semiconductor devices such as vacuum fluorescent displays, field emission displays [3], solar cells [4], magnetic [5], photoluminescent [6], electro-optical [7], etc. The ZnO can be synthesized by various methods, such as electrodeposition [8], evaporation [9], vapor-liquid-solid (VLS) growth [10], metal-organic catalyst, assisted vapor-phase epitaxy [11], aqueous thermal decomposition [12], microwave activated chemical bath deposition (MW-CBD) [13], chemical bath deposition (CBD) [14], surfactant-assisted hydrothermal method [15], and solution combustion method [16] [17]. This last method is more convenient than other because it is pensive, it has an easier composition control, and coating can be deposited on large area etc. Co-doping of host matrix is a technique for incorporating two or more elements into a host lattice with the objective of change sum or improves the properties physical and chemical of the host matrix. The ZnO has been co-doped with various elements (rare earth, lanthanides, metals, etc.) combined [2] [3] [4], in special with Cu2+ ions to tailoring the optical properties of Y3+ doped ZnO compounds because the Cu2+ ion has the capacity of: modify the luminescence of ZnO crystals by creating localized impurity levels [9] [18]. But also the Cu2+ ion can quench some emission photoluminescence type [19] as will be showed in this study. However, the doping of ZnO with Cu2+ ions cannot modify ZnO structure [20]. In turn, the Y3+ element belong to rare earth periodic family [5] [6], the importance of Y3+ is its capacity for tailoring the optical properties of ZnO, because Y3+ doping decrease the energy band gap of ZnO [7]. The Y3+ surface hinders crystalline growth and promotes vacancies generation [21]. In this experiment, the possible effects caused by the Cu2+ ions on the structural and optical properties of Y3+ doped ZnO compounds are analyzed and explicated. The Cu2+ + Y3+ co-doping process is realized by a solution combustion technique.

2. Experimental Details

2.1. The Solution Combustion Method

The experimental method of chemical synthesis solution combustion [17], is quite simple, fast and economical in which an oxidizer and a fuel agents are combined in a highly exothermic red-ox chemical reaction stoichiometric, producing ZnO, H2O (vapor), molecular N2, and CO2. In this work using Zinc Nitrate hexahydrate [Zn(NO3)2·6H2O] as oxidizer, urea [(H2NCONH2)] as fuel, yttrium chloride [YCl3] and copper chloride [CuCl2] as dopants, undoped and Cu2+ + Y3+ doped ZnO were synthesized by a solution combustion technique as a function of Cu2+ ion concentration in %wt, maintaining the Y3+ concentration constant in 3%wt. The samples were later annealed at 835˚C by 2 h.

2.2. Stoichiometric Equation

Pure and Cu2+ + Y3+ doped ZnO samples were obtained by a solution combustion technique by means of the following redox chemical reaction stoichiome-
The Equation (1) was obtained by taking into account the oxidizer/fuel molar ratio (O/F = 1) required for a stoichiometric mixture which is determined by summing the total oxidizing and reducing valences in the oxidizer compound and dividing it by the sum of the total oxidizing and reducing valences in the fuel compound [17]. Accordingly for the complete combustion of zinc nitrate-urea mixture, the molar ratio becomes 5/3, the equation balanced (1) was obtained with this value ratio. Using the weight atomic concept in Equation (1), it was used to obtain 3 gr. of ZnO for all the Cu$^{2+}$ ion concentrations. The dopants yttrium and copper by means its respective chloride were simultaneously integrated into ZnO host in each combustion reaction using the dopants concentrations correct. The samples produced were characterized by x-ray diffraction technique using a Philips PW 1800 diffractometer using Cu Ka radiation, the morphology of the samples was studied by means of a scanning electron microscopy JEOL JSM 840 A, and the photoluminescence spectra was recorded using a Tektronix 792 AD.

\[3\text{Zn}(\text{NO}_3)_2 \times 6\text{H}_2\text{O} + 5\text{H}_2\text{NCONH}_2 + 2(\text{YCl}_3 + \text{CuCl}_2)\]
\[\rightarrow 3\text{ZnO} + 10\text{H}_2\text{O} + 5\text{CO}_2 + 8\text{N}_2 + 2(\text{Cu}^{2+} + \text{Y}^{3+}) + 5\text{Cl}_2\] (1)

3. Results and Discussion
3.1. X-Ray Diffraction (XRD) Study
The XRD patterns of Y$^{3+}$ doped ZnO with 3%wt. and Cu$^{2+}$ + Y$^{3+}$ co-doped ZnO with 3%wt. of Y$^{3+}$ ion and 1, 3, 5, 10, and 20%wt. of Cu$^{2+}$ ion concentrations and after annealed at 835 °C by 2 h are showed in Figure 1. The observed XRD characteristic peaks positioned in 2θ scale at 31.64, (100), 34.32, (002), 36.02, (101), 47, 45, (102), 56.49, (110), 62.70, (103), 66.30, (201), 67.85, (112) and 69.93, (201) shows the good crystallinity of the material. All the diffraction peaks can be indexed to the hexagonal wurtzite structure of ZnO (JCPDS card No. 36-1451, a = b = 3.249Å, c = 5.206Å). However, other characteristic peaks at 29°, (222) and 27°, (230), corresponding to the yttrium oxide (Y$_2$O$_3$) and Y$_2$Cu$_2$O$_5$ phases respectively also were observed in Cu$^{2+}$ + Y$^{3+}$ co-doped ZnO, which can be attributed to the doping of Y$^{3+}$ ion into Zn$^{2+}$ lattice site. Also, it is observed that the peak intensity of the news phases decrease with Cu$^{2+}$ ion concentration until total quenching at 20%wt. due to Cu$^{2+}$ ion incorporation into Zn-Y-O lattice site and segregation of Y$^{3+}$ ion toward ZnO surface. The Y$_2$Cu$_2$O$_5$ phase also is obtained as secondary phase in the YBaCuO superconductor synthesis [22] [23] [24] [25]. The Figure 2 shows a magnification of the (002) plane between 34.1° and 34.7° in which are observed the changes in peak intensity and peak position as a function of Cu$^{2+}$ ion concentration. The peak intensity is increased when the Cu$^{2+}$ ion is incorporated into Y$^{3+}$-Zn-O lattice until 10%wt. Cu$^{2+}$ ion concentration. This is attributed to the Cu$^{2+}$ interstitial existence sharing the
Figure 1. XRD patterns of Y³⁺ doped (3%wt.) ZnO and Cu²⁺ + Y³⁺ co-doped ZnO as a function of Cu²⁺ ion concentration in %wt.

Figure 2. Red shift of the (002) enlarged plane as a function of Cu²⁺ ion concentration in %wt.

oxygen with the Zn²⁺ atoms increasing the peak intensity. After 10%wt. the peak intensity decrease, due to excess of Cu²⁺ atoms that are energetically efficient to coalesce into metallic copper cluster decreasing the peak intensity [20]. The peak position along (002) plane of Cu²⁺ + Y³⁺ co-doped ZnO samples is red shifted in 2θ scale and broader up to 10%wt. Cu²⁺ ion concentration, after this value the peak position is increased newly due to the effect by intercalation of Cu²⁺ ion on
the interatomic distance of the Y-Zn-O lattice [20]. The average crystal size of
the samples was obtained from diffraction (101) plane using the Debye-Scherrer
equation:

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

(2)

where \( \lambda \) is the X-ray wavelength used (1.5406Å), \( \beta \) is the full width at half maximum (FWHM) along (101) plane and theta is the Bragg diffraction angle. The Figure 3(a) and Figure 3(b) shows the change in FWHMH and average crystal

![Graph](image-url)

**Figure 3.** (a) FWHM; (b) average crystal size, as a function of Cu\(^{2+}\) ion concentration in %wt.
size as a function of Cu$^{2+}$ ion concentration respectively, it is observed from Figure 3(a) that the FWHM increases with Cu$^{2+}$ ion concentration until reach a maximum value at 10 %wt., after this value decrease until reach a value minimum. In contrary, from Figure 3(b) it is observed that the crystal size decrease with the Cu$^{2+}$ ion concentration until reach a minimum value in 10%wt. after this value the crystal size increase. This behavior between the FWHM and the average crystal size is predicted by the Debye-Scherrer equation, since for a maximum value of FWHM correspond a minimum value in crystal size. Also it is observed that the Cu$^{2+}$ + Y$^{3+}$ co-doped ZnO crystals have less size than Y$^{3+}$ doped ZnO; the initial reduction size from 75 nm with 0.0%wt. of Cu$^{2+}$ ion to 40 nm with 10%wt. of Cu$^{2+}$ ion is due to the distortion produced by Cu$^{2+}$ ions intercalated in the Zn-Y-O lattice [20]. At higher Cu$^{2+}$ concentration than 10%wt. the Cu$^{2+}$ atoms excess is combined forming the Y$_2$Cu$_2$O$_5$ compound.

3.2. Photoluminescence Study

The Figure 4 shows the photoluminescence (PL) spectra of pure ZnO and Y$^{3+}$ doped ZnO with 3%wt. The spectra were obtained in the UV-Vis range, illuminated with an excitation wavelength of 350 nm at room temperature. The PL spectrum of pure ZnO samples, exhibits the typical main band with characteristics peaks centered about 390 nm and corresponds to the near band edge (NBE) emission [6]. At higher wavelengths than NBE diffraction peak appears with less intensity that NBE peak the green emission band centered about 518 nm and attributed to free exciton recombination. From Figure 4 can be observed and calculated a little blue shift when Y$^{3+}$ dopant was incorporated into ZnO host lattice, changing the ultra-violet NBE emission from 390 to 382 nm increasing the ZnO band gap in 0.3 eV. This slight blue shift of the UV peak is caused by 3%wt. Y$^{3+}$ doping [9] and [16]. However it is observed an increase in UV intensity in Y$^{3+}$ doped ZnO compared with UV intensity of pure ZnO. The Figure 5 exhibit the room temperature PL spectra of Cu$^{2+}$ + Y$^{3+}$ co-doped ZnO samples with var-

Figure 4. Photoluminescence spectrum of pure ZnO and doped ZnO with 3%wt. Y$^{3+}$ ion. The samples were illuminated using a wavelength excitation of 350 nm.
ious Cu$^{2+}$ ion concentrations values of 2, 3, 5, 10 and 20%wt., it is clearly observed that for all Cu$^{2+}$ concentration the green PL emission due to free exciton recombination has been quenched by the intercalation of Cu$^{2+}$ ions into Y$^{3+}$ + ZnO host lattice; this quenching effect is attributed to a non-radiative recombination process known as non-radiative recombination Auger phenomena which is associated to degenerate electrons, in which the energy released by an electron is immediately recombined and absorbed by another electron and the energy involved is dissipated by phonons. Auger process is considered as the cause major of non-radiative recombination in semiconductor materials. Auger process depends on the doping atoms concentration and defects in the lattice. [19]. However, in Fig. 5 also it is observed that the UV-NBE emission of the samples is diminished by increasing Cu$^{2+}$ ion concentration, indicating that the optical-gap of ZnO semiconductor can be tailored by means of Cu$^{2+}$ doping. This last result can be technologically applied in UV radiation sensors fabrication [26].

3.3. Morphology Study

The scanning electron microscope (SEM) technique has been used to observe the surface morphology (SM) of the particles. The Figures 6(a)-(d) exhibits the SEM images of the SM of Cu$^{2+}$ + Y$^{3+}$ co-doped ZnO. The Figure 6(a) shows the SM of Y$^{3+}$ doped ZnO sample, it presents the existence of like-ovoid particles compact, dense structure and forming layers which have its surface covered with grains of size similar that are unevenly distributed. The average size grain is of 30 nm. The Figure 6(b) shows the SM of Cu$^{2+}$ + Y$^{3+}$ co-doped ZnO with 2%wt. of Cu$^{2+}$ ions concentration, it is observed that the grains are most agglomerated.
Surface morphology of Cu$^{2+}$ + Y$^{3+}$ doped ZnO as a function of Cu$^{2+}$ ion concentration in %wt. and 3% of Y$^{3+}$ fixed. and evenly distributed in the sample. In this case the grains have an average size of 50 nm. The Figure 6(c) exhibits the SM of the Cu$^{2+}$ + Y$^{3+}$ co-doped ZnO with 3%wt. of Cu$^{2+}$ ions concentration. It is seen that further increase in the intercalation of Cu$^{2+}$ ions into Zn-Y-O host lattice improves the crystallinity of the sample. The Figure 6(c) displays the SM of Cu$^{2+}$ + Y$^{3+}$ co-doped ZnO with 3%wt. of Cu$^{2+}$ ions, the particles presents like-spheres form and higher size than Y$^{3+}$ doped ZnO. The average grain size of these particles is 50 nm. Finally the Figure 6(d) exhibits the SM of Cu$^{2+}$ + Y$^{3+}$ co-doped ZnO with 10%wt. of Cu$^{2+}$ ions concentration. In this Cu$^{2+}$ concentration level is observed the presence of the Y$_2$Cu$_2$O$_5$ as is corroborated by the XRD patterns showed in Figure 1. However, also can be seen Cu$^{2+}$ ions interstitial localized into ZnO matrix. The geometry of these particles is like-spheres with an average size of 75 nm.

4. Conclusion

In this study, pure and Cu$^{2+}$ + Y$^{3+}$ co-doped ZnO were synthesized as a function of Cu$^{2+}$ ion concentration by a solution combustion method. The XRD study showed that the hexagonal wurtzite structure of ZnO is maintained after Cu$^{2+}$ doping process. Using the (002) plane of XRD spectra, a red shift was observed due to Cu$^{2+}$ doping process. The PL results for Y$^{3+}$ doped ZnO showed a UV intensity higher compared with the UV intensity of pure ZnO. For all the Cu$^{2+}$ ion concentrations, the green PL emission is quenching by Cu$^{2+}$ doping effect. The
UV PL emission can be tailored by Cu$^{2+}$ doping effect. In 10%wt. of Cu$^{2+}$ doping, the Y$_2$Cu$_2$O$_5$ phase is created. A blue shift of 0.3 eV is observed in the UV PL emission of Cu$^{2+}$ + Y$^{3+}$ samples due to Cu$^{2+}$ doping effect.

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