Quenching Photoluminescence of Eu(III) by Cu(II) in ZnO:Eu³⁺+Cu²⁺ Compounds by Solution Combustion Method

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Abstract

In this study Cu²⁺+Eu³⁺ co-doped ZnO(ZnO/Cu²⁺+Eu³⁺) solid solution powders were synthesized by solution combustion method using as oxidant agent zinc nitrate hexahydrate and as fuel urea; the Cu²⁺ concentrations were 0, 1, 2, 3, 10, and 20 %Wt; the Eu³⁺ ion concentration was fixed in 3%Wt. The samples after were annealed at 900°C by 20 h in air. The structural results showed the largely presence of a wurtzite solid solution of Cu²⁺+Eu³⁺doped ZnO, at high Cu²⁺ doping CuO and Eu₂CuO₄ phases are also present. Morphological properties were analyzed using scanning electron microscopy (SEM) technique. However it is important to remark that the Cu²⁺ ions suppress the Eu³⁺ ion photoluminescence (PL) by means of an overlap mechanism between Cu²⁺ absorption band and Eu³⁺ emission band (e.g. ⁵D₀→⁷F₂) of the Eu³⁺ emission spectra.

Keywords

ZnO, Co-Doped Cu²⁺+Eu³⁺, Quenching, Photoluminescence, Solution, Combustion

1. Introduction

Zinc oxide (ZnO) is actually considered to be a II-VI semiconductor material of great importance in basic science as in technologic applications due to its important properties physical and chemicals: the ZnO has a band gap energy of 3.7 eV [1]-[6], an large exciton bonding energy of 60 meV, also has defects as O and Zn vacancies; however it is chemically and thermally stable and friendly with the environment. Due to these properties, the ZnO can be utilized in the fabrication of devices such as: electro-optical devices [7], gas sensors [8], catalyst [9], piezoelectric device [10], electro-optical [11], photovoltaic [12], paramagnetic [13], etc. Several methods for
the production of ZnO undoped and doped with various types of dopants (rare heart, metals, lanthanides, etc.) [14]-[17] have been described, such as, electrodeposition [18], evaporation [19], vapor-liquid-solid (VLS) growth [20], metal organic catalyst assisted vapor-phase epitaxy [21], aqueous thermal decomposition [22], microwave activated chemical bath deposition (MW-CBD) [23], chemical bath deposition (CBD) [24], surfactant-assisted hydrothermal method [25], solution combustion [26] etc. This last method is more convenient than other because it is very fast, and less expensive; it has an easier composition control, and coating can be deposited on large area etc. The introduction of Cu$^{2+}$ ions into ZnO lattice sums or produces changes that improve the ZnO properties such as: band gap tailored, magnetic and electrical properties, passivation of defects, as p-type dopant in the original n-type ZnO semiconductor. However, actually it is well known that the co-doping with Cu$^{2+}$ ion in Eu$^{3+}$ doped glasses photoluminescent compounds the Cu$^{2+}$ ion can quench the Eu$^{3+}$ photoluminescence [27]-[29] with the increase of the Cu$^{2+}$ ion concentration in glasses matrix; this quenching effect can be used to tuning between ultra-violet and visible emission in devise photoluminescent. In this study co-doped ZnO/Cu$^{2+}$ + Eu$^{3+}$ solid solution powders have been synthesized by solution combustion method as a function of the Cu$^{2+}$ ion concentration in %Wt. maintaining the Eu$^{3+}$ ion concentration constant at a value of 3% Wt. Finally the sample was annealed at 900°C by 20 h. Also it is demonstrated that the quenching Eu$^{3+}$ PL by the copper ion action also occurs in ZnO matrix.

2. Experimental

The synthesis method solution combustion is simple and fast caused by the chemical reaction oxidation-reduction (REDOX) highly exothermic (1200°C) [18] between an oxidizer agent and a fuel, in this experiment Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) was used as oxidizer agent and urea (NH$_2$CONH$_2$) as fuel, copper chloride (CuCl$_2$) and Europium chloride (EuCl$_3$) were used as dopants agents. The next chemical reaction (REDOX) between the oxidizer agent and the fuel is an reaction highly exothermic and is the Stoichiometric reaction obtained with a equivalence ratio value of unity (i.e. $f = O/F = 1$) where O and F are the total oxidizing and total reduction valences of the components and the energy released by the combustion is at maximum [18]. With this reaction are obtained the follow products: ZnO, H$_2$O (vapor), CO$_2$, and N$_2$.

$$3\text{Zn(NO}_3\text{)}_2\cdot\text{6H}_2\text{O} + 5\text{H}_2\text{NCONH}_2 \rightarrow 3\text{ZnO} + 16\text{H}_2\text{O} + 5\text{CO}_2 + 8\text{N}_2 + \text{heat}$$ (1)

Using the atomic weight concept, the Equation (1) was translated to grams/mol and used to obtain 3 gr of ZnO powder. The Cu$^{2+}$ ion dopant concentration values were 0, 1, 2, 3, 10, and 20 wt%. The Eu$^{3+}$ ion dopant concentration was maintained constant at 3 Wt% with respect to 3 gr of ZnO. From the translated grams/mol Equation (1) (no shown), 8.31 gr of Zn(NO$_3$)$_2$·6H$_2$O, 3.68 gr of H$_2$NCONH$_2$ plus the numerous of grams corresponding to each Cu$^{2+}$ ion concentration plus 3 Wt% Eu$^{3+}$ ion were mixing with 20 ml of H$_2$O and stirring vigorously in a flask glass and after put on a hot plate at 500°C, after of few minutes the reactive solution boils, foams, ignites, and burns with an incandescent flame at an approximate temperature of 1200°C [18] producing 3 gr of ZnO powders approximately. After all the samples are annealing at 900°C by 24 h. The ZnO/Cu$^{2+}$+Eu$^{3+}$ samples thus obtained were structurally characterized by X-ray diffraction (XRD) technique using a Philips PW 1800 diffractometer with Cu k$_\alpha$ radiation (1.5406 Å), the photoluminescence (PL) of the ZnO/Cu$^{2+}$+Eu$^{3+}$ samples was studied by means of a spectrophotometer Fluoro Max-P that uses a xenon lampas excitation source, The wavelength excitation was of 270 nm, and finally, the morphology of the ZnO/Cu$^{2+}$+Eu$^{3+}$ powders was record using a scanning electron microscopy (SEM) JEOL JSM 840 A.

3. Results and Discussion

3.1. Structural Characterization

The Figure 1 shows the X-ray diffractograms of the ZnO/Cu$^{2+}$+Eu$^{3+}$ powders as a function of the Cu$^{2+}$ ion concentration and annealing at 900°C by 20 h. From the XRD patterns, can be observed that for the Cu$^{2+}$ concentrations of 1, 2, 3, 10 and 20%Wt all the diffraction peaks can be indexed to the majority phase hexagonal wurtzite type ZnO structure for all samples (JCPDS card #89-(102)), also, for the Cu$^{2+}$ ion concentrations of 1, 2, 3 and 10%Wt a peak at $2\theta = 28.5^\circ$ is present and is assigned to the minority Eu$_2$O$_3$ phase (JPDAS card #86-2476). The diffractograms also reveal the high crystallinity of the product for the five Cu$^{2+}$ ion concentrations, for the higher Cu$^{2+}$ concentrations of 10 and 20%Wt. A peak corresponding to the Eu$_2$CuO$_4$ molecules is present; effectively:
in Figure 2 can be see the peak at the 2theta scale at 24° correspond to the Eu$_2$CuO$_4$ phase, however also in Figure 2 appear all the peaks characteristic of the zinc oxide majority phase reported in this text.

Comparatively, contrary to the observation of Iribarren et al. [17] obtained from your experiments on Cu$^{2+}$ doped ZnO, in our diffractograms can be not observed a little shift initially toward higher angles of the principal peak (101) until 3% Wt of Cu$^{2+}$ where an maximum is reached, after at higher Cu$^{2+}$ concentrations the angular displacement is toward lower angles, in the first case this is due to the substitution of the Zn ion with 0.06 nm size by the smaller Cu$^{2+}$ ion with 0.057 nm size that cause an lattice parameter shrinkage, in the second case this is attributed to an relative saturation of the Cu$^{2+}$ ions on the samples surface, in our case the the not presence of angular changes can be due to the Eu$^{3+}$ ions present in the ZnO lattice. No diffraction peaks were detected from other impurities. Using the Scherrer formula, the average crystallite size calculated from characteristic peak (101) was 160 nm for the ZnO intrinsic and decreased to 150 nm for the ZnO/Cu$^{2+}$/Eu$^{3+}$ samples doped with 10 Wt% of Cu$^{2+}$ ion concentration.

![Figure 1. XRD spectra of the Cu$^{2+}$/Eu$^{3+}$ doped ZnO as a function of the Cu$^{2+}$ ion concentration in %Wt.](image1)

![Figure 2. XRD diffractogram of the ZnO and Eu$_2$CuO$_4$ compound. Cu$^{2+}$ ion concentration for this figure was of 20 wt%.](image2)
3.2. Morphological Study

The Figure 3(a) shows the SEM image of the form of the Eu$^{3+}$ doped ZnO whit out Cu$^{2+}$ ions, it is observed that the Eu$^{3+}$/ZnO crystallites are agglomerated forming amorphous particles of 1.5 µm of large in an approximation. The Figure 3(b) shows the SEM image of a particle of Cu$^{2+}$+Eu$^{3+}$ doped ZnO polycrystalline particles, it can be see that the individual crystallites are agglomerated forming amorphous particles whit 2 µm side and 3 µm of large approximated.

3.3. Photoluminescence Study

The Figure 4(a) and Figure 4(b) shows the room temperature photoluminescence spectra (PL) of the Eu$^{3+}$ doped ZnO without the Cu$^{2+}$ ion dopant and of the Cu$^{2+}$+Eu$^{3+}$ doped ZnO (ZnO:Cu$^{2+}$+Eu$^{3+}$) nanocrystals as a function of the Cu$^{2+}$ ion concentration in Wt% and after both samples undoped and doped with the Cu$^{2+}$ were annealing at 900°C by 24 h, the samples were irradiated with an excitation wavelength of 270 nm (in the UV range). In Figure 4(a) it is observed that the PL spectra correspond to the Eu$^{3+}$ ion emission in a ZnO matrix, in particular the most intense peak at the visible color red whit 613 nm in wavelength [27]. However it is observed from Figure 4(b) that the ZnO:Cu$^{2+}$+Eu$^{3+}$ samples doped with 1, 2, 3, 10, and 20 Wt% are all alike: because they does not present antypical green broad emission band from 400 nm to 600 nm centered about 516 nm [28] as is showed in Figure 4(a), this band is due to the intrinsic defects emission of ZnO host. However, in the PL spectra of the ZnO:Cu$^{2+}$+Eu$^{3+}$ samples two peaks at the UV region in 350 and 380 nm are present, in this the intensity of this last peak I this observer that your intensity it is decreased at an concentration of 20% Cu$^{2+}$, this decrease is due to the capacity of Quenching of the Cu$^{2+}$ at hide concentration the first peak is attributed to the 5d→7f europium transition, the second band is attributed to near edge band (NEB) emission [29], other peak at the violet-blue region centered about 420 nm also is observed, this peak is due to the 5D→4F Eu$^{3+}$ transition. From the photoluminescence spectra corresponding to the Eu$^{3+}$ ion also appear: the peaks at 591, 613 and 630 nm are related to the direct intra-4f transitions in Eu$^{3+}$ ions 5D$^0$→7F$^j$ (j = 1, 2, 3), the most intense emission is associated to the 5D$^0$→7F$^2$ transition in the red spectral region (613 nm) and is due to a allowed electric-dipole transition with inversion antisymmetric [28] [30], which results in a large transition probability in the crystal field [31]-[34]. The peak at 591 nm is due to the 5D$^0$→F$^1$ transition, is an allowed magnetic-dipole transition. The peak at 579 nm is due to the forbidden 5D$^0$→F$^0$ transition due to the same total angular momentum, indicating that some Eu$^{3+}$ ions possibly occupy other sites as interstitial sites [35]-[38]. It is very important to note from the photoluminescence spectra that as increase the Cu$^{2+}$ ion concentration in the ZnO:Cu$^{2+}$+Eu$^{3+}$ samples the intensity of the most intense transition of the Eu$^{3+}$ ion with red wavelength of 613 nm decrease until an negligible value while the intensity of the wavelength emission at 380 nm situated in the UV region increase until...
reach an constant value for high Cu\textsuperscript{2+} ion concentrations: effectively: the Figure 5 shows the emission intensity variation of the red $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of the Eu\textsuperscript{3+} ion and of the UV emission peak at 380 nm of the ZnO:Cu\textsuperscript{2+}+Eu\textsuperscript{3+} samples as a function of the Cu\textsuperscript{2+} ion concentration, the graphic shows that as the Cu\textsuperscript{2+} ion concentration increase the red color intensity decrease until an minimum value while the intensity of the UV emission increase until obtain an constant value. It has been reported that divalent copper ion can effectively suppress Eu\textsuperscript{3+} photoluminescence, in an matrix of glass this is due to the quenching effect of Cu\textsuperscript{2+} impurities on Eu\textsuperscript{3+} emission photoluminescence quenching resulting from Eu\textsuperscript{3+} → Cu\textsuperscript{2+} non-radiative energy transfer in which an spectral overlap occurring between Cu\textsuperscript{2+} absorption and Eu\textsuperscript{3+} emission(e.g. $^5\text{D}_0 \rightarrow ^7\text{F}_2$) transition occur \cite{28} \cite{29}. Thus, in this paper is postulated that the quenching of the Eu\textsuperscript{3+} photoluminescence also can occur in ZnO matrix.

Figure 4. (a) Photoluminescence spectra of Eu\textsuperscript{3+} doped ZnO at 3%Wt; (b) Photoluminescence spectra of Cu\textsuperscript{2+}+Eu\textsuperscript{3+} doped ZnO as a function of the Cu\textsuperscript{2+} ion concentration in %Wt.

Figure 5. Intensity of the emissions Wavelength 380 and 613 nm as a function of the Cu\textsuperscript{2+} ion concentration in %Wt.

4. Conclusion

In this study Cu\textsuperscript{2+}+Eu\textsuperscript{3+} doped ZnO solid solution powders were synthesized by solution combustion method maintaining the Eu\textsuperscript{3+} ion concentration fixed at 3%Wt and after annealing at 900°C by 24 h. From the XRD study it is confirmed that the ZnO hexagonal wurtzite structure is conserved after the introduction of the Cu\textsuperscript{2+} ion in the ZnO structure, and the same XRD study showed the presence of the minority phases Eu\textsubscript{2}O\textsubscript{3} and Eu\textsubscript{2}CuO\textsubscript{4}. From photoluminescence study it is demonstrated that the Cu\textsuperscript{2+} ion effectively suppresses the Eu\textsuperscript{3+} ion
photoluminescence due to the PL quenching effect of the Cu$^{2+}$ ion on the Eu$^{3+}$ ion.

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