

Influencia of the Cu Ion on the Structural and Optical Properties in Cu + Ce Co-Doped ZnO Compounds

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Abstract

This article showed and explained the effects of the Cu^{2+} ions on the structural and photoluminescent properties of Ce^{3+} doped ZnO compounds (ZnO: Ce^{3+}) in $\text{Cu}^{2+} + \text{Ce}^{3+}$ co-doped ZnO ($\text{ZnO: Cu}^{2+} + \text{Ce}^{3+}$) solid solutions powders. The samples were synthesized by a solution combustion method maintaining the Ce^{3+} ion concentration constant in 3%wt and varying the Cu^{2+} ion concentration in 0%wt, 1%wt, 2%wt, 3%wt, 10%wt and 20%wt. However, pristine ZnO and Ce^{3+} doped ZnO were synthesized by the same method for comparison. After the synthesis process all the samples were annealed at 900°C by 24 h. The pure ZnO, ZnO: Ce^{3+} and ZnO/ $\text{Cu}^{2+} + \text{Ce}^{3+}$ powders were structurally characterized using X-ray diffraction (XRD) technique, the XRD patterns showed that for either undoped and doped with the Cu^{2+} ion both exhibited the hexagonal wurtzite ZnO crystalline structure, also the diffraction peaks of both samples types showed a little change toward lesser angles. The morphology and particle size of the samples were observed by means of a scanner electron microscopy (SEM); from SEM imagen is observed that the crystallites of the samples are agglomerated forming cage-like hollow structures caused by the combustion process. The cage-like structures have approximate size of 800 nm. In addition, the photoluminescence of pure ZnO, ZnO: Ce^{3+} and ZnO: $\text{Cu}^{2+} + \text{Ce}^{3+}$ compounds was measurement as a function of Cu^{2+} ion concentration under a excitation wavelength of 378 nm in the UV region. As an important result, it is observed that by Auger phenomena of non-radiative recombination, the UV emission of the ZnO is quenching.

Keywords

Zinc Oxide, Copper-Cerium, Co-Doped, Solution-Combustion

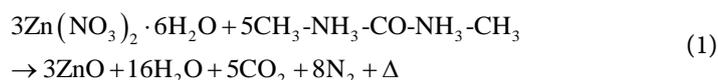
1. Introduction

Actually, there are a lot of scientific literature on the II-VI semiconductor material zinc oxide (ZnO) produced by researchers dedicated to the physical optical study in all the world, because the ZnO has singular and extraordinary physical and chemical properties: presents a wide direct band gap of 3.37 eV at room temperature [1] and has bonding energy of 60 meV that makes ZnO very apt for exciton-based applications [2]. However, such properties make to the ZnO a very versatile material ideal for working in conjunction with other materials. The ZnO has been studied in basic and technological applications: fabrication of the follow devices: electro-optic [3], solar cells [4], piezo-electric [5], magnetic [6], gas sensors [7], photoluminescent [8], etc. The ZnO can be synthesized using various methods, such as: magnetron sputtering [9], chemical vapor deposition (CVD) [10], Co-precipitation [11], metalorganic [12] and solution combustion (SC) technique [13]: this last method is very fast, less expensive, easier variables deposit control, very efficient and highly reproducible. In this work we used SC as synthesis method. In other hand, the Cu atoms incorporation into the crystalline lattice of the ZnO leads to change or improvement in some properties of the ZnO material such as: band gap tailored, electric, magnetic, electronic, thermoluminescent, surface defects control, structural, and photoluminescent [14] [15] [16] [17]. Furthermore, the Cu ion has been used to quenching the Eu^{3+} PL in glasses and ZnO matrix [18] [19]. In addition, specifically, the ZnO can be doped with various elements of the periodical table (lanthanides, earth rare, metals, phosphorous, etc.) for changing the ZnO intrinsic PL emission spectra as well as its emission intensity [20] [21] [22] [23]. Between the ZnO dopants the most prominent is the cerium atom (Ce^{3+}), the first element of the lanthanide series due to its high PL emission efficiency and wide versatility: according to the studies realized by various researchers [24]-[29], from your experimental results the authors show that the Ce^{3+} doped ZnO can presents anomalous PL emission spectra: from the UV radiation until the red color emissions; this multiple color PL emission is attributed to the Ce^{3+} ion and also depend of the excitation radiation of illumination. In this work, pure ZnO, Ce^{3+} doped ZnO and $\text{Cu}^{2+} + \text{Ce}^{3+}$ co-doped ZnO solution powders were synthesized by a solution combustion technique. The $\text{ZnO}/\text{Cu}^{2+} + \text{Ce}^{3+}$ compound was synthesized as a function of the Cu^{2+} ion concentration in %wt. maintaining constant the Ce^{3+} ion concentration at 3% wt. The three type's samples were annealed at 900°C by 24 h. Structurally the samples were characterized by means of X-ray diffraction (XRD) technique. Your photoluminescence properties were studied by measuring its PL under an excitation wavelength of 378 nm at room temperature.

2. Experimental Details

The chemical synthesis technique by solution combustion is possible thanks to the development of a chemical reaction of oxidation-reduction (REDOX) between an oxidizer agent and a fuel, the reaction is highly exothermic (1200°C) [30] producing oxides metallic, water vapor, carbon-dioxide and nitrogen mo-

lecular. In our experiment zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was used as oxidizer agent and urea (5H NCONH) as fuel. In the following chemical REDOX reaction:



The Equation (1) is the stoichiometric form of the REDOX reaction obtained with a equivalence ratio value of unity (*i.e.* $f = \text{O}/\text{F} = 1$) where O and F are the total oxidizing and total reduction valences of the agents and the energy released by the combustion is at maximum [30]. Using the Equation (1), intrinsic ZnO, Ce^{3+} doped ZnO and $\text{Cu}^{2+} + \text{Ce}^{3+}$ co-doped ZnO solid solution powders were synthesized and after annealed at 900°C by 24 h. The source of the dopants Cu^{2+} and Ce^{3+} were copper chloride (CuCl_2) and cerium oxide Ce_2O_3 respectively. The Ce^{3+} ion concentration was fixed at 3%wt, while the Cu^{2+} ion concentration takes the values of 0%wt, 1%wt, 2%wt, 3%wt, 10%wt and 20%wt. The pure ZnO, ZnO/ Ce^{3+} , and ZnO/ $\text{Cu}^{2+} + \text{Ce}^{3+}$ samples thus obtained were structurally characterized by X-ray diffraction (XRD) technique using a Philips PW 1800 diffractometer with Cu $\text{K}\alpha$ radiation (1.5406 \AA), the morphology of the powders samples was recorded using a scanning electron microscopy (SEM) JEOL JSM 840. The PL study was realized using a spectrofluorometer Fluoro Max-P that uses a xenon lamp.

3. Results and Discussion

3.1. Structural Study

The **Figure 1** shows the XRD patterns of the as prepared samples of ZnO, ZnO: Ce^{3+} and ZnO: $\text{Cu}^{2+} + \text{Ce}^{3+}$ as a function of the Cu^{2+} ion concentration in %wt.

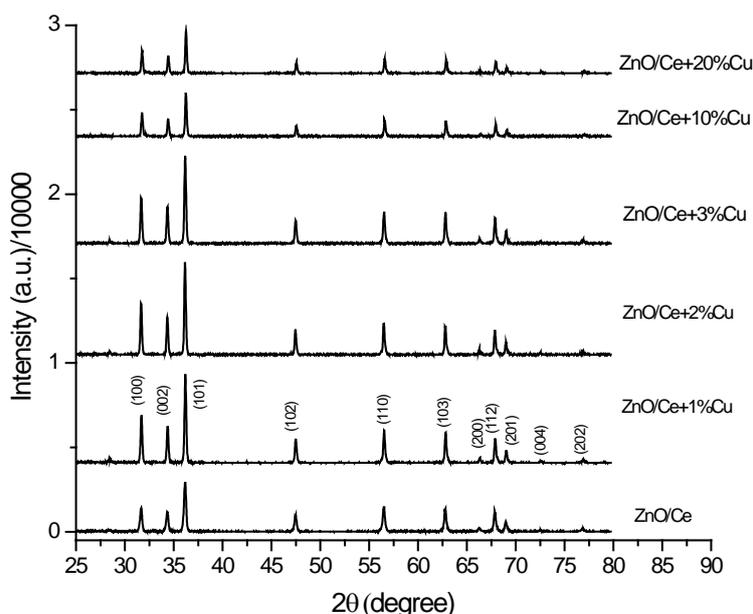


Figure 1. XRD pattern of ZnO, Ce^{3+} doped ZnO and $\text{Cu}^{2+} + \text{Ce}^{3+}$ co-doped ZnO as a function of the Cu^{2+} ion concentration.

and annealed at 900°C by 24 h. From the XRD patterns can be observed that all the diffraction peaks can be indexed to the hexagonal wurtzite ZnO structure (JCPDS CARD #89-(102)), no change of the peaks toward lesser angles was observed: the Cu^{2+} ion incorporation into the ZnO crystalline lattice do not changed the ZnO basic structure. However, the **Figure 2** shows the XRD pattern of the ZnO joint to two diffraction peaks at 28.4° and 32.5°: the first is assigned to the residual Ce_2O_3 phase and the second to the CuO compound. Also is observed that the diffraction peaks are very sharp indicating good crystallization of the products. By using the Scherrer formula the size of the crystallites was estimated in 60 nm.

3.2. Morphology Study

The **Figure 3** shows the SEM micrographs images of (a) undoped ZnO, and doped ZnO with (b) 3, (c) 10, and (d) 20%wt of Cu ion concentration and 3%wt of Ce ion respectively. For undoped ZnO it is observed that the powders presents particles with amorphous morphology and connected each other forming large network systems with irregular pore sizes and shapes. In Cu + Ce doped ZnO the powders shows cages broken structure with hollows formed by scaping gases during the combustion process. This porous system with lot of voids is typical of solution combustion synthesized powders caused by scaping gases. In higher Cu doping the SEM micrograph also shows the presence of various small crystalites with different sizes and shapes within grains this is due to the non-uniform distribution temperature and mass flow in the combustion flame.

3.3. Photoluminescence Study

The effects of the incorporation of the Cu^{2+} ion in the lattice crystalline of the Ce doped ZnO matrix on the luminescence of the $\text{Cu}^{2+} + \text{Ce}^{3+}$ co-doped ZnO powders were studied measuring the photoluminescence (PL) of the samples. The PL was obtained at room temperature under the excitation wavelength of 378 nm

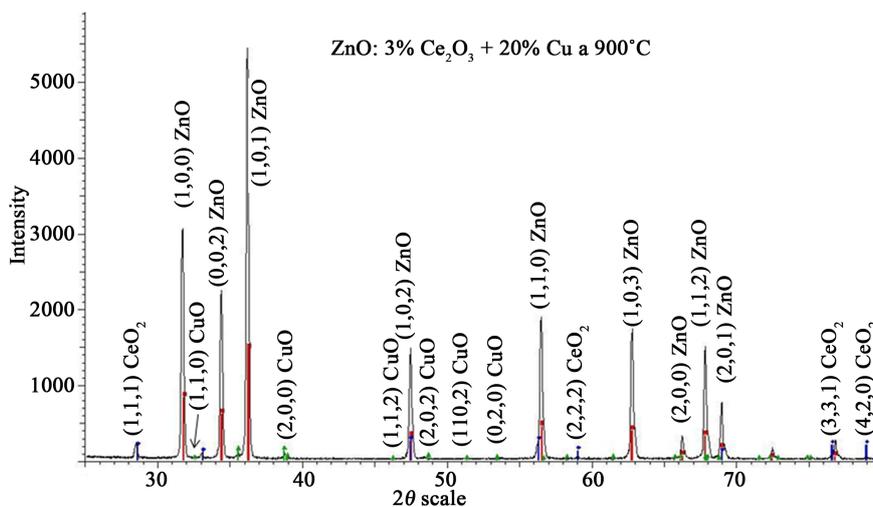


Figure 2. XRD patterns of ZnO, Ce_2O_3 and CuO compounds.

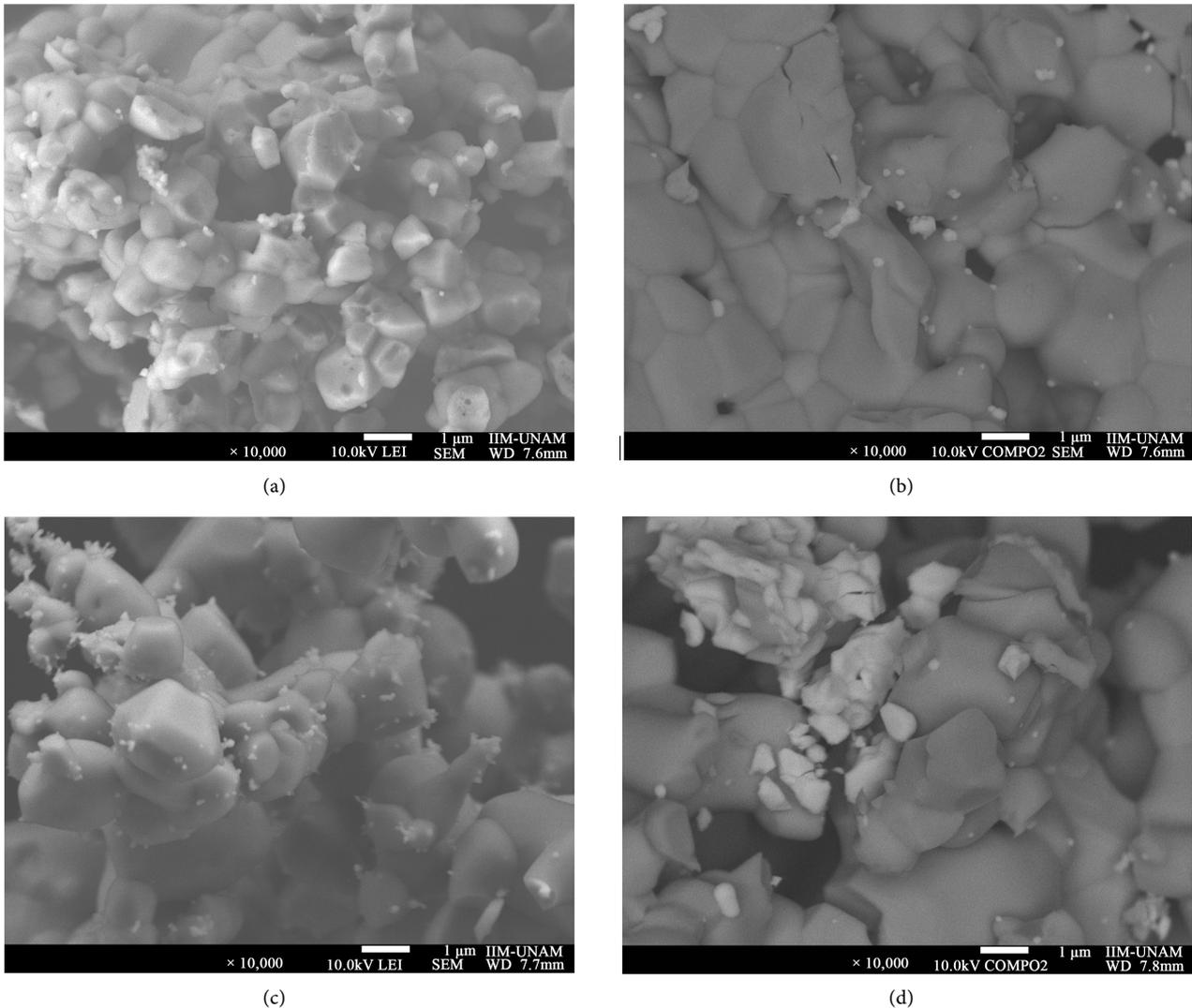


Figure 3. SEM micrographs of the (a) Ce^{3+} doped ZnO, ZnO: 3%Ce intrinsic; (b) $\text{Ce}^{3+} + 2\text{Cu}$, ZnO: 3%Ce + 2%Cu; (c) ZnO: 3% Ce^{3+} + 10%Cu; and (d) $\text{Ce}^{3+} + 20\text{Cu}$, ZnO: 3%Ce + 20%Cu.

obtained from a He-Cd laser. The **Figure 4** exhibits the PL spectra of the ZnO: $\text{Cu}^{2+} + \text{Ce}^{3+}$ compounds as a function of the Cu^{2+} ion concentration in %wt. In **Figure 4** appears four relevant emission peaks for all Cu^{2+} ion concentration centered about 422, 470, 640 and 665 nm. The first two peaks belong to the blue color region and are attributed to the electric-dipole-allowed transition of the Ce^{3+} ions [31]. The second two peaks are centered in the redcolor region, and are due to a radiative recombination process that occurs between the donors associated with oxygen vacancies O_v and the acceptors associated with the native defects adjacent to the Cu^{2+} impurity [32]. It is important to note from **Figure 4** that the UV PL was quenching of the PL spectra; this quenching effect is caused by a non-radiative recombination process known as non-radiative Auger recombination phenomena [33] 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 [21], and [22]. Auger

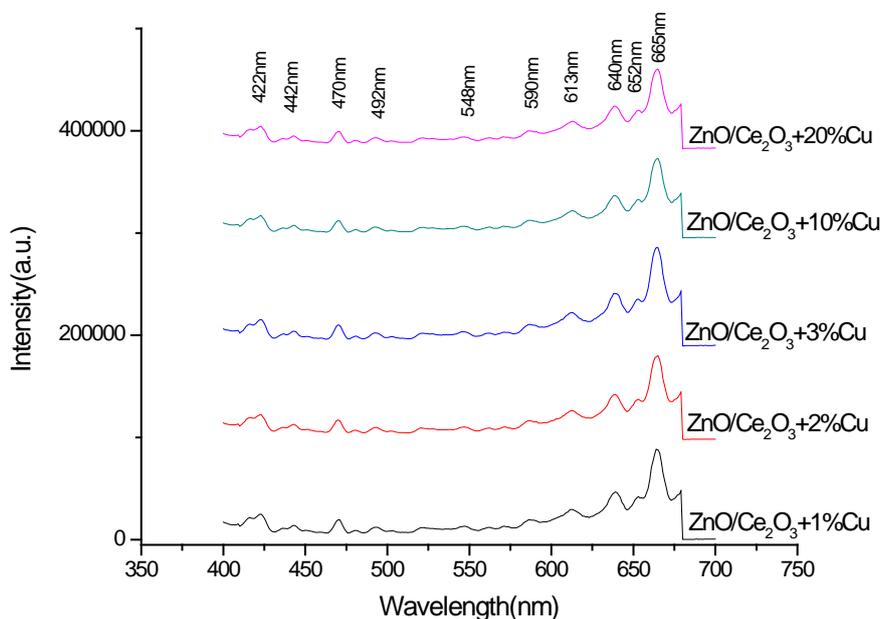


Figure 4. PL spectra of the ZnO: Ce³⁺ + Cu²⁺ samples as a function of the Cu²⁺ ion concentration in %wt.

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 [34]. In our case, when the ZnO: Ce³⁺ powders are doped with a minimum of Cu²⁺ atoms (<1%wt) the near band edge emission (NBE) origin of the UV PL in the ZnO semiconductor is quenching in its totality.

4. Conclusion

In this work the effects caused by the Cu²⁺ ion on the structural and optical properties of co-doped compounds type ZnO: Cu²⁺ + Ce³⁺ synthesized by a solution combustion method have been investigated. It is found that the copper ion presence does not change the ZnO crystalline structure. The PL emission spectra consist of four relevant peaks: two peaks centered in the blue color region attributed to an electric-dipole-allowed; and the other two peaks centered in the red color region due to radiative recombination between donor-oxygen vacancies defects and the acceptors Cu²⁺ impurity. However, it is concluded that the Cu²⁺ ion introduction into the ZnO crystalline lattice quenches the UV PL of the ZnO semiconductor matrix caused by a non-radiative-recombination Auger effect; this result can be technologically used to fabric devices photoluminescent with ZnO matrix without UV emission.

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