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Investigation of additional Raman modes in ZnO and $Eu_{0.01}Zn_{0.99}O$ nanoparticles synthesized by the solution combustion method

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ABSTRACT

In this study, we report on the origin of Raman additional modes (AM) in ZnO and $Eu_{0.01}Zn_{0.99}O$ nanoparticles (NPs) synthesized by the solution combustion method (SCM). The as-produced samples were thermally annealed at different temperatures and under different conditions (air, N_2-flow and He-flow). The as-produced NPs exhibited the characteristic color (salmon) of N-doped ZnO. Typical patterns of ZnO wurtzite were found by X-ray diffraction data and no evidences of additional phases were detected. Raman spectra of as-produced ZnO and $Eu_{0.01}Zn_{0.99}O$ NPs showed AM features usually found in N-doped ZnO. These features disappeared after thermal annealing in air, but they do not disappeared after thermal annealing in N_2- and He-flow. Effects of Eu-doping on AM modes were observed, indicating that co-doping with Europium can be used to increase the Nitrogen solubility in ZnO. Using the Raman data the maximum N-content in $Eu_{0.01}Zn_{0.99}O$ NPs was estimated in 10^{18} cm^{-3}. Our results concerning thermal annealing at different conditions indicated that it is unlikely that Zn_i-O_i complexes are the origin of the ~510 cm^{-1} AM, as it is currently proposed in the literature. Instead, the Raman AM features observed in this study were attributed to disorder activated Raman modes favored by N-doping.

1. Introduction

Zinc oxide (ZnO) has been extensively investigated over the years due to its unique physical properties, which include wide direct band gap (~3.37 eV at 300 K) and large exciton binding energy (60 meV). These two characteristics make ZnO very much attractive from the standpoint of technological applications, especially in ultraviolet light-emitting diodes, lasers, solar cells, and UV photodetectors [1]. In addition, ZnO is considered a promising material for spintronics [2] since it was predicted and experimentally confirmed the existence of room temperature ferromagnetism (RTFM) in transition metal (TM) and rare-earth (RE) doped ZnO [3,4]. Despite the large number of publications in RTFM, many points are still unclear, particularly whether the phenomenon is an intrinsic property of TM and RE-doped ZnO or simply a result of the formation of secondary magnetic phases. This is likely to be the source of magnetic ordering verified in many cases [2,5]. Furthermore, the very possibility of obtaining reproducible *p*-type-conductivity is also under debate [1].

Production of *p*-type doped ZnO is a key point for device fabrication based on this material platform. However, ZnO naturally exhibits *n*−type conductivity due to Oxygen vacancies (V_O), Zinc interstitials (Zn_i) and Hydrogen impurities which make it very difficult to obtain both types of conductivity. Doping of ZnO with Nitrogen has been considered one of the best approaches to solve this issue, as Nitrogen has size and electronic structure comparable to Oxygen [2]. Nevertheless, Nitrogen has low solubility in ZnO and therefore many different synthesis and doping experimental routes have been tested. Among them, the solution combustion method (SCM) is considered a promising alternative [6–8]. The SCM is one of the simplest techniques used to synthesize doped ZnO nanoparticles (NPs). SCM uses a fast and self-sustaining chemical reaction between metal salts and an organic fuel, usually urea. The SCM route is not expensive and allows good control of the stoichiometric composition and crystalline size of the as-produced NPs.

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Furthermore, SCM do not use neither toxic reagents nor complicated steps or high reaction temperatures, it is suitable for large scale production and can be employed for a huge number of elements [4]. However, despite the advantages offered by the SCM approach the amount of Nitrogen that can be introduced into the ZnO structure is not clear yet [7,8].

Another key point, still under debate in the literature, is the origin of five Raman additional modes (~275, ~510, ~580, ~640, and ~855 cm^{-1}) observed in most N-doped ZnO [9–11] and also found while introducing other doping elements (Fe, Sb, Al, and Ga) [12–15]. Despite the question on whether the Raman additional modes (AMs) could appear or not through doping with atoms other than Nitrogen, many explanations have been proposed to describe the origin of these features. The most common explanation is the association with local vibrational modes (LVM) of Nitrogen in ZnO [7,11,16]. On the other hand, Manjón et al. [17] attributed these Raman AMs to disorder-activated B_1 silent modes whereas Friedrich et al. [18] ascribed the Raman AMs at 273.9 cm^{-1} and 509.5 cm^{-1} to vibrations of an interstitial Zn-atom bound to a substitutional N-atom (Zn_i-N_O) and vibrations of Zn_i-O_i complexes, respectively. Other explanations in the literature are disorder or defects favored in the presence of Nitrogen and resonantly enhanced LO scattering [2].

In this study, we investigated the presence of Raman AMs in ZnO and $Eu_{0.01}Zn_{0.99}O$ nanoparticles (NPs) synthesized by the SCM method. To this aim different experimental techniques were used to assess information regarding the doping of the ZnO NPs, such as scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and Raman spectroscopy.

2. Experimental procedure

The SCM was used to synthesize ZnO and Eu-doped ZnO ($Eu_{0.01}Zn_{0.99}O$) NPs starting with analytical grade europium nitrate ($Eu(NO_3)_3.9H_2O$), zinc nitrate ($Zn(NO_3)_2.6H_2O$) and urea ($CO(NH_2)_2$) as fuel. All reagents were purchased from Across (New Jersey, USA) while manipulations and reactions were carried out in air. The stoichiometric composition of all mixtures was calculated such that the total oxidizing and reducing valences of the oxidizer and fuel were balanced and the energy release was maximized for each reaction. For the elements H, C, Eu, Zn, O and N the corresponding valences used were +1, +4, +3, +2, −2 and 0, respectively, as it is usual in propellant theory [19]. Nitrogen valence is taken as zero because of its conversion to molecular Nitrogen (N_2) during combustion. Thus, the total valences in $Eu(NO_3)_3.9H_2O$ (−15) and $Zn(NO_3)_2.6H_2O$ (−10) should be balanced by the total valences in the fuel, which adds up to +6. Hence, in order to release the maximum energy for the reaction the stoichiometric composition of the redox mixture requires 1.67 mol of $CO(NH_2)_2$.

All the reactants were hand mixed in a wide-mouth vitreous silica basin of 300 mL and heated up to ~400 °C on a hot blanket. This process was performed inside a fume-cupboard under ventilation. With the rise in temperature, the reactants melted and became an opaque liquid that began frothing. Then, ignition took place characterized by a rapid increase in temperature and the release of a large quantity of gases. The reactions lasted for a few seconds and produced a dry and very fragile foam, which could be transformed into powder at the slightest touch. In this report, the samples resulting from the combustion process, but not submitted to a post thermal annealing, were labeled “as-produced”. For the post-treatment, part of the as-produced ZnO and Eu-doped ZnO nanoparticles were thermally annealed in a resistive furnace under air atmosphere at a heating rate of 2 °C/min up to 700, 800, 900, and 1000 °C. The samples were maintained at the annealing temperature for 2-h and then cooled down slowly to room temperature. The same process was performed separately in He- and N_2-gas flow up to 800 °C for part of the as-produced nanopowders. The gas flow was supplied at 1 L/min in a tube furnace.

The samples' morphology and chemical composition were assessed using a SEM (JEOL JEM 840A) equipped with an EDS accessory. For these measurements, the samples were coated with a Platinum film. Additionally, the samples were characterized by XRD using a Rigaku diffractometer (model Ultima IV) equipped with CuKα radiation ($\lambda_{mean} = 1.5418$ Å) and operating in the range of $20^\circ \leq 2\theta \leq 80^\circ$, with a scanning rate of 0.5°/min and steps of 0.05°. The resulting data were analyzed by the Rietveld method using the EXPGUI-GSAS software [20]. The Raman system employed to record the spectra was a commercial triple spectrometer (Jobin Yvon Model T64000) equipped with a charge-coupled device (CCD) detector. The optical source used was the 532 nm line from a Verdi − V5® laser operating at 0.10 mW. All experimental data were recorded at room temperature.

3. Results and discussion

Fig. 1 shows SEM images and EDS plots of ZnO and $Eu_{0.01}Zn_{0.99}O$ NPs. Only Zn, Eu, O and Pt were detected while the Pt EDS features originate from the samples' processing for SEM and EDS experiments. The observed quantitative analysis is in accordance with the nominal values for the samples, with roughly 50% (Zn and O) for ZnO NPs and 1% (Eu), 49% (Zn) and 50% (O) for $Eu_{0.01}Zn_{0.99}O$ NPs. As the SCM uses nitrates as reagents and urea as fuel it is very likely the presence of Nitrogen as impurity in our samples. Should

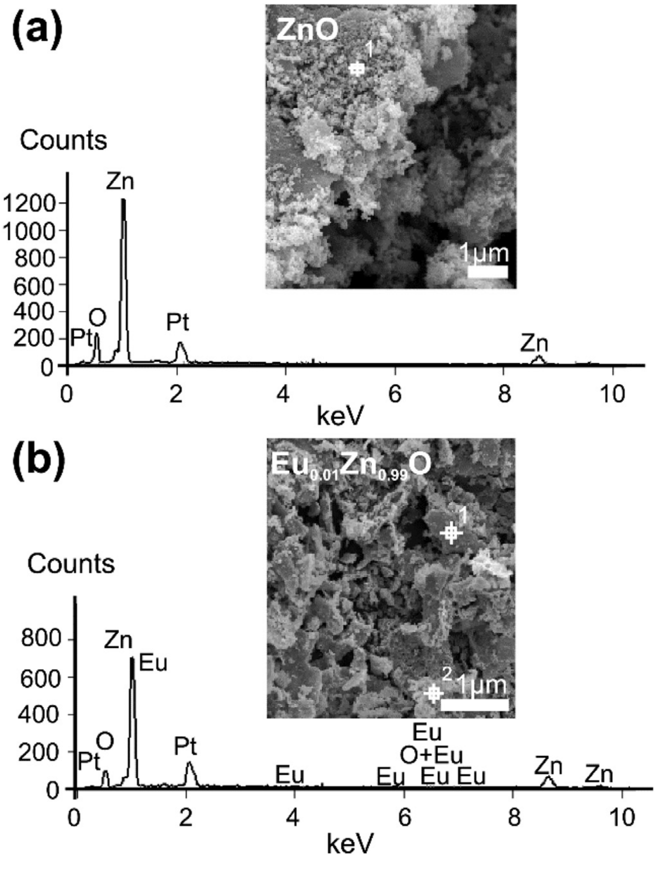

Fig. 1. EDS spectra and SEM images of as-produced (a) ZnO and (b) $Eu_{0.01}Zn_{0.99}O$ NPs. Open square-crossed marks in the micrographs show points where the EDS spectra were recorded.