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Full Length Article

Synthesis and Optical Properties of Pb Doped ZnO Nanoparticles

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ABSTRACT

This article deals with the structural and optical characterization of lead-doped zinc oxide nanoparticles synthesized by precipitation method. X-ray diffraction study confirmed the substitution of Pb dopant without disturbing the basic wurtzite structure of zinc oxide. The average crystallite size, lattice constants, and unit cell volume also increased up to 10% of lead doping. The energy gap of the samples was determined from the ultraviolet-visible absorption spectrum as well as Tauc's plot which infers that the energy gap decreases with the increase of lead content. Fourier Transformation Infra Red spectrum confirmed the lead dopant through peak shifting from 437–549 cm^{-1}. Photoluminescence spectrum also defines the leads dopant by means of intensity increase. Scanning electron microscope study also confirmed the existence of particles in nanometer size and it witnessed the microstructure transformation from nanoparticles to the rod-like structure on 10 (wt.%) lead doping.

1. Introduction

Zinc oxide (ZnO) is a versatile II–VI group direct band gap semiconductor having a wide band gap of 3.37 eV with the large excitonic binding energy of 60 meV [1–3] at room temperature [4–6]. In recent years, ZnO nanocrystals gained renewed interests due to its distinctive optical, electronic, and chemical properties that are required for fabrication of nanoscale electronic and optoelectronic devices and chemical sensors [7–10]. The large exciton binding energy of 60 meV ensures an efficient ultraviolet (UV) and blue emissions at room temperature. It is reported [11] that ZnO possesses (i) higher quantum efficiency, (ii) good stability against photo-corrosion and photochemical properties, (iii) ability to grow a high-quality single crystal at low cost. Also, it is an inexpensive luminescent and bio-friendly oxide semiconductor material. As a result, ZnO is expected to have an extensive applications in UV lasers, biosensors, bio- imaging, drug delivery, piezoelectric transducers, dye-sensitized solar cells, high sensitivity chemical gas sensor, volatile organic compound sensor, DNA sequence sensor, short wavelength (green, blue, UV) optoelectronic devices, light emitting diodes and field-effect transistors [12]. Recent development in nanotechnology uses the ZnO nanostructure as a cantilever in scanning electron microscope with size 500 times smaller than the conventional cantilever, which offers improved sensitivity and mechanical flexibility [13].

In recent years, tuning the energy gap of ZnO semiconductor material has fascinated the attention of researchers on account of the enhancement in their properties as well as the development in the device performance. This development is talented by fine-tuning of its band gap by doping with a variety of transition metals (TM) like Fe, Co, Ni, Cu, Cd, Hf and Ag and also by doping with post-transition metals like Bi, Pb, and Al *etc*. Among these elements, lead (Pb) is a suitable dopant for reducing the band gap of ZnO [14] By suitably varying the stoichiometry ratio of the Pb dopant, energy gap of the ZnO semiconductor material can be reduced and we can get a new material with different properties as compared to their intrinsic complement.In this context, nano-sized Pb doped ZnO nanomaterials have attracted tremendous attention [15,16].

Literature survey shows that different synthesis methods have been adopted for the synthesis of Pb doped ZnO nanoparticles, including sol-gel technique, microemulsion synthesis, mechanochemical processing, spray pyrolysis and drying, thermal decomposition of organic precursor, RF plasma synthesis, supercritical-water processing, self assembling, hydrothermal processing, vapour transport process, sonochemical or microwave-assisted synthesis, direct precipitation and homogeneous precipitation method. For instance, Ramin Yousefi et al., [17] has investigated Pb doped ZnO nanowires synthesized by a thermal evaporation method and studied their morphology and optical properties. They found that Pb doping lowers the crystalline quality of the ZnO nanowires. Similarly, Mashkoor Admad et al., [18] also investigated Pb doped ZnO nanowires synthesized by the same thermal evaporation method. They found that the morphology of doped nanowires is like a cantilever however they observed a red

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shift in the UV-Vis spectrum due to the merge of impurity levels with the edge of the conduction band. *Likewise*, Kannadasan et al., [19] has synthesized Pb doped ZnO nanocrystals by simple chemical precipitation method and studied their optical and electrochemical characteristics. They found that Pb has some influences on controlling the size and morphology of ZnO. Following this, Inigo Valan et.al [20] has studied the characteristics of Pb doped ZnO thin film deposited by Spray Pyrolysis method. They found the optical and structural properties of ZnO are modified by Pb doping and the transmittance increases in the near infrared region (800–1100 cm^{-1}) as the doping percentage is increased. Also, they claimed the increase in the energy gap of ZnO from 3.27 to 3.36 eV. These literature surveys clearly reveal three major things (i) the reports available on Pb doping in ZnO nanopowders using chemical route is scanty. (ii) Pb doing in ZnO is very difficult due to *p*-type impurity and (iii) we need to use some expensive method like discussed above. As a challenge, we preferred precipitation method for Pb doping in ZnO. Because, precipitation method results in atomic scale mixing and hence, the annealing temperature required for the formation of the nanoparticle is low, which lead to smaller particles. So, we have chosen the precipitation method.

In this article, we focus on the synthesis of ZnPbO nanoparticles by chemical precipitation method. $Zn_{1-x}Pb_xO$ samples were synthesized with different '*x*' values ranging from 0, 2, 5, 8 and 10 (wt.%). Influence of Pb doping on structural and optical properties of ZnO nanoparticles have been studied by x-ray diffraction (XRD) method, Fourier transform infrared (FTIR)spectroscopy, Ultraviolet–visible (UV–vis) spectroscopy, Photoluminescence (PL) spectroscopy, Scanning electron microscopy (SEM) with compositional analysis and Transmission electron microscope (TEM). We found that the crystallite size reduced from 32 nm to 24 nm with Pb doping. A redshift of about 0.1 eV in energy gap was observed with Pb doping from $x = 0$ to 10 (wt.%). In the PL spectrum, the intensity of UV emission was suppressed with an increase of Pb concentration but its position remained unchanged. The novelty of the present work is the absence of any secondary phase till 10 (wt.%) and the microstructure transformation from nanoparticle to nanorods.

2. Experimental Procedure

2.1. Sample synthesis

Zinc acetate dihydrate [$Zn(CH_3COO)_2{\cdot}2H_2O$](99.0% purity), Lead acetate dehydrate [$Pb(CH_3COO)_2{\cdot}2H_2O$] (99.5%purity) and sodium hydroxide [NaOH] pellets (99.0% purity) were procured from Sigma-Aldrich. All chemicals were directly used without further treatment. Undoped ZnO and Pb doped ZnO nanopowders were synthesized by a simple chemical precipitation route, as described elsewhere [21] using a mixture of lead acetate and zinc acetate in ethanol and distilled water.

In a typical synthesis, $Zn_{1-x}Pb_xO$ (where $x = 0$, 2, 5, 8 and 10 wt %) samples were synthesized by adding the appropriate amount of $Pb(CH_3COO)_2{\cdot}2H_2O$ to the [$Zn(CH_3COO)_2{\cdot}2H_2O$)] in the mixture of 50 ml distilled water and 50 ml ethanol. The weight ratio of Pb and Zn [$x = Pb/(Zn + Pb)$] was kept at about, 0,2, 5, 8, and 10 for preparing undoped and Pb doped ZnO samples. At the same time, 2 g of NaOH pellets were dropped into the 50 ml mixed solution of distilled water and ethanol. Thus prepared NaOH solution was heated up to boiling temperature and the lead acetate dihydrate and zinc acetate dehydrate mixed solution was dropped slowly into the NaOH solution for 1 h and then cooled to room temperature (40 °C). The solution turned into a milky white and the precipitation was formed in the solution. Then 3 ml of polyethylene glycol (MW: 400) was added as a capping agent. Following this, the precipitate was kept in an ultrasonic bath for 30 min and then allowed to settle down the particles for 7 days at room temperature. Then the particles were repeatedly washed with ethanol to remove unwanted ions, and the obtained white precipitate was dried at 100 °C). overnight in a vacuum oven to get Pb-doped ZnO nanopowders. Finally, the powder samples were annealed at 350 °C) for 4hrs.

2.2. Characterization

Crystal structure identification was performed using an x-ray diffractometer (XRD: Philips Analytical Model No.-PW1830) equipped with Ni-filtered CuKα radiation (λ = 1.54187 Å) for 2θ = 10 - 80°, with a scanning rate of 1°/min, operated at 40 kV/30 mA. Surface morphology and microstructure of the particles was studied by using JEOL scanning electron Microscope (JEOL SEM-Japan) operated at 20 kV/20 mA and the chemical composition was examined with Energy-Dispersive X-ray Spectrometer (EDS: INCAPentaFETx3, Oxford Instruments, UK).JEM-1010 transmission electron microscope (TEM) was used to study the microstructure and size of the nanoparticles. For TEM analysis the sample was ultrasonically dispersed in ethanol, and then a drop of a substance was placed on amorphous carbon films supported by the copper grid and dried in air. To identify the functional groups and to confirm the substitution of Pb ions, the samples were examined with Fourier Transform Infrared Spectrometer (FTIR; RX1 PERKINELMER: USA) at a resolution of 2 cm^{-1}. The measurements were carried out in the region 400–4000 cm^{-1} using KBr as the beam splitter. Optical absorption measurements in the UV-Visible range were performed at room temperature using a Lambda 35 (PERKINELMER: USA) spectrophotometer. The wavelength range used in the experiment was 200 to 1100 nm. For this study, the powder samples were dispersed in deionized water and mixed well. Photoluminescence (PL) measurement was carried out by means of PL spectrometer (Kimon, SPEC-14031K, Japan) with a He-Pb laser line of 320 nm as the excitation source.

3. Results and Discussion

3.1. Phase analysis from XRD pattern and Debye–Scherer plot

X-ray diffraction analysis is a powerful tool to estimate the lattice constant and average crystallite size, and whether the samples possess single phase or multi-phase. XRD pattern of the annealed $Zn_{1-x}Pb_xO$ (where $x = 0$, 2, 5, 8 and 10 wt.%) nanoparticles is shown in Fig. 1. The peaks were analyzed using Powder X software which shows that all the samples are in single phase with hexagonal wurtzite structure (space group $P6_3mc$). The dominant peaks appear at 2θ ~31.8°, 33.4°, 36°, 47.5°, 56.5°, 62.8°, 66.3°, 67.9°, 69°, 72.6° and 76.9° corresponds to (100), (002),(101), (102), (110), (103), (200), (112), (201), (004) and (202) planes of the hexagonal wurtzite structure and there are no characteristic peaks related to Pb metal or PbO secondary phases. As seen, the peaks of the Pb substituted ZnO samples show an insignificant shift of the middle of the diffraction peaks towards a higher angle with respect to that of the undoped ZnO sample. The slight shift of the XRD peaks with the Pb doped ZnO represents that Pb has been effectively doped into the ZnO host structure at the Zn site. Here, it can be seen that addition of Pb concentration doesn't affect the crystalline quality of ZnO. We observed the most intense peak around 36° in all the samples which imply that the ZnO and Pb substituted ZnO nanoparticles have a preferred growth orientation along ≪101≫> direction. XRD pattern also indicates that the intensity of diffraction peaks increases with a decrease in FWHM (not shown in table) with doping concentration which is the identification of enhancement of crystallinity and increase in crystallite size. All the diffraction peaks observed is in good agreement with standard diffraction data (JCPDS Card no.:

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