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Luminescence properties and decay kinetics of nano ZnO powder doped with cerium ions

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ABSTRACT

ZnO nanopowders doped with cerium ions (1.2 and 1.5 at. wt.%) were synthesized through soft solution route using ultrasound. Sonication has been found to be an effective way for doping rare earth ions like cerium into ZnO. This was confirmed from energy dispersive analysis of X-rays (EDAX) measurement. Further, optical absorption and photoluminescence (PL) measurements corroborate this finding. X-ray diffraction (XRD) studies show the increase of crystallite size and unit cell volume with doping of cerium ions. Formation of fibrous structure of ZnO:Ce was observed from the transmission electron microscopy (TEM) measurements. Although the structural measurements indicate Ce^{4+} ion occupying substitutional site in ZnO, PL and absorption studies confirmed the presence of Ce^{3+} ion in the powder. The coexistence of Ce^{3+} and Ce^{4+} ions has been explained on the basis of conversion of Ce^{3+} to Ce^{4+} in the oxidizing environment. Thermoluminescence (TL) and photo-stimulated decay of luminescence (PSDL) decay studies give an idea of various trapping levels present in the band gap of ZnO. These traps release electrons during optical stimulation to give bimolecular kinetics in nano ZnO:Ce powders.

1. Introduction

Study of nano semiconducting ZnO doped with various impurities has resulted in several publications leading to books [1–5], reviews [6–11] and papers [12–21]. But the role of impurities and vacancies in this system has not been understood clearly. It is well known that vacancies and defects play an important role in photoluminescence (PL) and thermoluminescence (TL) of inorganic insulating oxides [22]. It is also well established that the decrease in crystallite size leads to changes in optical, electrical and sensing properties of nanopowders. In a small nanoparticle, large number of atoms will be situated either at or near the free surface. When the size of the particle is of the order of 5 nm, 30–50% of the atoms are influenced at the surface compared to a 100 nm particle where this remains to few percent. Such structural differences in nano regime are expected to give rise to exciting optical, structural and thermal properties which are different from bulk. Studies on semiconducting oxides like ZnO, TiO_2 and In_2O_3 have been reported with PL measurements (2,3,7,12,16). However, TL studies are rather scare and scanty. Studying the defect properties through PL, TL and optically stimulated luminescence OSL techniques have become standard tools to characterize alkali halides and insulating oxides doped with all types of impurities [10,11,22]. In the case of nanocrystalline powders and thin films doped with rare earth ions, TL studies are not enough to draw any conclusion. Lanthanide impurities in semiconductor quantum dots have been considered as promising candidates for making light emitting diodes (LED). GaN doped with rare earth impurities like Eu, Sm, Pr and Tm have been studied by Hori et al. 2004 [23]. ZnO ($Eg=3.37$ eV at room temperature) is a promising material when compared with GaN. Thus, the present investigation aims at finding out the structural and optical properties of nano ZnO powders doped with cerium. Cerium, being a rare earth ion has the propensity to capture both electron and holes and can exist as Ce^{4+} or Ce^{3+} thus making the study more interesting and important.

2. Materials and method

$(Zn(NO_3)_26H_2O)$ and $(Ce(NO_3)_36H_2O)$ of AR grade having 99.99% purity were taken as starting material and dopant sources respectively. These were dissolved in distilled water and the resulting solution was stirred continuously with the help of a

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magnetic stirrer. Liquid ammonia solution having 25% of NH_3 concentration was added drop by drop to this solution till a clear solution was obtained. The resultant solution was placed inside a sonicator (model: VC-375, Sonic and Material Inc.) operated at 112.5 W. The frequency of the sonicator was maintained at 20 KHz $\pm$ 50 Hz. Sonication process was carried out continuously for 3 h after which white precipitates were observed to settle down in the bottom of the container. The pH of the solution was measured before and after the process of sonication and has been given in Table 1. The precipitates were collected through centrifugation and washed four times with distilled water and finally with acetone. Then these powders were dried at 100 °C for 2 h inside an oven operated at ambient pressure. In this process ZnO and ZnO doped with cerium (1.2 and 1.5 at. wt.%) were prepared. The chemical reactions taking place during the sonication process can be enumerated as given below.

$$NH_3 + H_2O \rightarrow NH_3.H_2O \rightarrow NH_4^+ + OH^-$$

$$Zn(NO_3).6H_2O \rightarrow Zn^{2+} + 2NO_3^- + 6H_2O$$

$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O$$

$$Ce(NO_3)_3.6H2O \rightarrow Ce^{3+} + 3NO_3^- + 6H_2O$$

$$Ce^{3+} + 4OH^- \rightarrow CeO_2 + 2H_2O + e^-$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$$

These powders were subjected to X-ray diffraction (XRD) in a Panalytical Xpert-Pro diffractometer to ascertain their crystal structure. Williamson–Hall (W–H) method was applied to calculate the strain value using XRD data. All measurements were carried out at room temperature ($\approx$ 26 °C). Scanning electron microscope (SEM-Hitachi-S-3400 N) and transmission electron microscope (TEM, Technai G^2, FEI, Netherlands) were used to study the structure and morphology of the crystallites. Energy dispersive analysis of X-rays (EDAX) and selected area electron diffraction patterns (SAED) were also obtained from the TEM. A Shimadzu UV-1700 spectrophotometer was used to record the optical absorption spectra of the powders in the range between 300 and 800 nm. The absorption measurements were carried out by dissolving the powders in acetone and dispersing them using a sonicator. Photoacoustic (PA) spectral measurements were carried out using a PerkinElmer FTIR spectrometer (Model: Spectrum GX) in the range between 400 cm^{-1} and 4000 cm^{-1} in transmittance mode. For this a special attachment from M/s Harricks was used. Photoluminescence (PL) measurements of the powder samples were carried out at room temperature ($\approx$ 26 °C) with the help of a Fluoromax-4 (PerkinElmer) spectrofluorometer. The powder samples were excited at 293 nm and 354 nm and the emission spectra were recorded. Thermoluminescence measurements were carried out by using a commercial TL/OSL reader (model no: Risø TL/OSL reader TL-DA-15). Beta (β) irradiation with an inbuilt (^{90}Sr) source was performed at room temperature at a dose rate of 0.084 Gys^{-1}. The details of the experimental set up and procedure has been described by Gartia et al. [24]. The heating rate used for the TL measurement was 5 °Cs^{-1}. After subtraction of the background noise, the data were plotted. For optical-stimulation, the β irradiated nanopowders were kept in the same chamber used for TL measurements. The stimulating light was a blue photon source and the excitation of the defect centers were carried out for 30 s after which the decay measurements were recorded through the electronic system.

Table 1
Time period of sonication and pH value of reaction for synthesis of ZnO and ZnO:Ce samples.

Sample name	Time of sonication	Initial pH	Final pH
ZnO	120 min	9.8	7.5
ZnO:Ce (1.2 at. wt.%)	170 min	10.1	7.7
ZnO:Ce (1.5 at. wt.%)	180 min	10.3	7.8

3. Results

The X-ray diffraction patterns of ZnO and ZnO doped with cerium (1.2 and 1.5 at. wt.%) have been depicted in Fig. 1A. The 'd' and 'I' values of the patterns were matched with the powder diffraction standard data files. The major phase was found to be ZnO (wurzite) (card no-005–0664) with a small amount of $Zn(OH)_2$ (card no-76–1778). Formation of $Zn(OH)_2$ was observed to decrease with the increase in cerium content in ZnO. This indicates the inhibition of $Zn(OH)_2$ phase in the presence of cerium ions. No separate phase for cerium oxide was observed in this XRD pattern. The crystallite sizes for ZnO and ZnO:Ce (1.2 and 1.5 at. wt.%) were calculated from W–H plot given in Fig. 1B. The crystallite size was found to be large compared to that of undoped sample (Table 2). Strain values were also calculated from the W–H plot and have been given in Table 2. It can be seen that strain value increases for ZnO:Ce samples. ZnO unit cell volume was found to be 47.2457 $Å^3$. This value increases to 47.2677 $Å^3$ and 47.2851 $Å^3$ for ZnO doped with 1.2 and 1.5 at. wt.% of cerium respectively. The lattice parameters calculated from XRD data have also been given in the same table.

Surface structure plays an important role in determining the electrical and optical properties of nanomaterials. Accordingly,

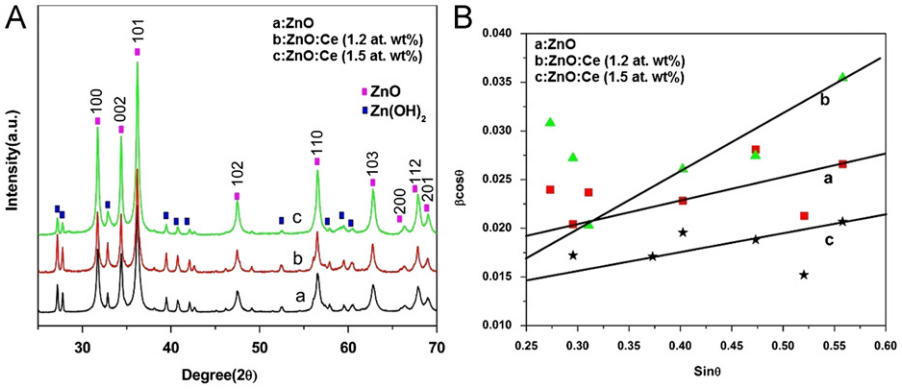

Fig. 1. (A) X-ray diffraction patterns of (a) ZnO, (b) ZnO:Ce (1.2 at. wt.%) and (c) ZnO:Ce. (1.5 at. wt.%). (B) Williamson–Hall plot of (a) ZnO, (b) ZnO:Ce (1.2 at. wt.%) and (c) ZnO:Ce (1.5 at. wt.%).