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Nanostructures of Lead Doped Zinc Oxide: Synthesis and Characterization

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Lead doped ZnO nanocrystallites have been synthesized in the laboratory using low temperature chemical precipitation technique. Precursor was prepared using absolute ethanol, zinc acetate and lead acetate in fixed proportions. Precipitates were obtained by adding 0.14 M LiOH into the precursor solution. Scanning electron microscopy images were obtained for studying morphology of the synthesized doped nanophosphors. Photoluminescence in the visible region has been recorded. Owing to increased quantum efficiency, these nanophosphors can be utilized for various industrial applications such as coating materials for fluorescence tubes, optical memories, bio-sensors, active medium for laser oscillations.

Key Words: Doped ZnO nanocrystallites, Excited state lifetimes, Trap-depth values.

INTRODUCTION

Zinc oxide is important luminescent material because of its high luminescence efficiency, non-ohmic properties, large binding energy, and lasing at room temperature[1-7]. Various chemical synthesis methods had been reported in literature to synthesize the nanostructures such as solvothermal, hydrothermal, self-assembly and sol-gel[8-13]. Earlier Vanheusden *et al.*[14] had reported that doping of Pb in ZnO may form a separate PbO phase. Further, they had shown that Pb also causes strong sub-gap absorption in the zinc oxide grains to 2 eV and due to limited solubility of the substitution Pb in the zinc oxide lattice, the excessive Pb precipitates into a separate PbO like phase most likely in the grain boundaries. However, Ohasi *et al.*[15,16] had used PbO and PbF_2 as flux for crystal growth of zinc oxide in bulk. Interest of using Pb as a dopant is that it may help in formation of long length crystalline nanobelts of ZnO. In the present investigations, a new type of nanometer-scale structure: such as nanobelts that could be the basis for inexpensive ultra-small sensors, flat-panel display components and other electronic nanodevices, have been synthesized in the laboratory. This paper describes a low temperature synthesis method of and their characterization.

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EXPERIMENTAL

Synthesis of long length ZnO lead doped nanobelts[17] were carried out using chemicals zinc acetate, lead acetate and absolute ethanol. Alcohols are commonly used because the solvent also acts as a reagent. However, the solvent does not participate in the reaction forming ZnO from zinc acetate[18,19]. The synthesis of nanobelts involves co-precipitation reaction of inorganic precursors of Zn^{2+} and O^{2-} with dopant ions in aqueous medium of absolute ethanol. The concentration of Pb impurity in the solution was maintained at various atomic percentage with Zn^{2+}, for ZnO: Pb samples. For 0.1M Zn^{2+}; 21.95 g of zinc acetate has been dissolved in 1000ml of absolute ethanol. Then 3.793 g of lead acetate has been dissolved in 100 mL of absolute ethanol to obtained 0.1 M solution of Pb^{2+}. In typical synthesis 100 mL of 0.1 M zinc acetate solution is mixed with 0.1 M solution of lead acetate with desired atomic percentage prepared in absolute ethanol. Then it was refluxed for 3 h under magnetic stirring at 80°C. Then the precursor was mixed with 0.14 M LiOH prepared in 100 mL of triply deionized water. Immediately precipitate formation starts, which were kept at 4°C for few hours and then the precipitates, were separated out using centrifugal machine (5000 rpm, 5 min) at –10°C. Centrifugation at low temperature results in higher yield and uniform ribbon-like nanostructure of ZnO nanobelts[5,6]. The Precipitates were washed several times with distilled water. Then Precipitates were dried in oven at a temperature of about 80°C. Scanning electron microscope images of the samples were obtained from JSM-6100 type microscope. Lifetime measurements have been carried out using a pulsed nitrogen laser as an excitation source with output wavelength 337.1 nm and high peak output power *ca.* 200 kW per pulse. The short-lived photoluminescence from the sample at an angle of 90° to the laser beam was collected by a fast photo-multiplier tube; a detector through an assembly of monochromator; a wavelength selective element and glass slab; UV radiation filter. The multi-exponential PL decay signals from the phosphors were recorded and analyzed to calculate life-time values. The multi-exponential decay curves have been peeled-off into three components by the method of Bube using computer simulation[20,21].

RESULTS AND DISCUSSION

ZnO nanobelts with various concentrations of Pb impurity (varying from 5 to 20 at. %) have been characterized using scanning electron microscope and time resolved laser induced photoluminescence (TRPL). Scanning electron microscopic images (Fig. 1A) reveal long length nanobelts ranging to a few micrometers in length.

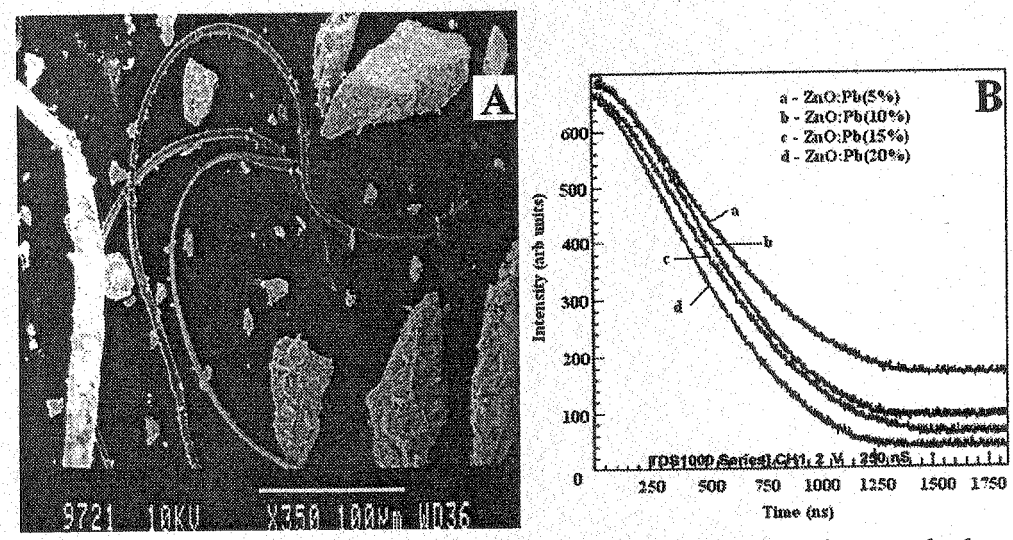

Fig. 1. A) Scanning Electron Micrographs of ZnO: Pb nanobelts
B) Multi-exponential luminescence decay curves of Pb doped ZnO nanobelts

Fig. 1B indicates the luminescence decay curves of various Pb doped ZnO nanobelts with concentrations of Pb varying from 5 to 20 %. The intensity of luminescent radiation at time't' is given as

$$I = I_0 e^{-pt} \tag{1}$$

where I_o is the intensity of radiation at cut-off position and the constant 'p = $1/\tau$' is the transition probability of the corresponding radiative transition. 'τ' is lifetime of excited state from where photoluminescence is monitored by fast PMT; the time spent by the electron in the trap before recombination. A plot of Ln (I) *vs.* time will be a straight line in case of single trap of energy (E) From the slope of line, which provide the value of 'p', one can calculate value of trap-depth, E, according to the Boltzmann's equation[20,22]

$$p = S e^{-E/kT} \tag{2}$$

where S is escape frequency factor $\left(\sim 10^9\ s^{-1}\right)$, k is the Boltzmann's constant and T, the absolute temperature. Life-time and trap-depth values simulated from the time resolved multi-exponential decay curves are mentioned in Table 1 using eqs. 1 and 2. Three components of the life-time values are observed because of multi-exponential nature of the decay curve of sized ZnO nanophosphors. Decrease in life-time values are observed with increase in concentration of Pb in ZnO semiconductor. The minimum life time value has been observed to be 638 ns in case ZnO:Pb (20 %). Addition of a catalyst stops isotropic agglomeration of particles, alternatively an anisotropic agglomeration occurs in nanowires or nanobelts[19]. LiOH (0.14 M) gives nearly neutral nanobelts (pH = 8.0)[17]. It is clear from the scanning electron microscopic images that nanobelts are highly crystalline. Enhancement of blue emission demonstrates that ZnO nanobelts absorb energy from the excited source and transfer it non-radiativly to the luminescence centers

of lead ion. Life-time shortening takes place with increase in impurity concentration

TABLE- 1
LIFE-TIME, TRAP-DEPTH AND EMISSION WAVELENGTH VALUES OF LEAD DOPED ZnO NANOBELTS

Phosphors: Impurity	Lifetime values (ns)			Trap depth values (eV)			Emission Wavelength (nm)
	τ_1	τ_2	τ_3	E_1	E_2	E_3	λ
ZnO:Pb (5%)	855	1072	1480	0.175	0.181	0.189	438
ZnO:Pb (10%)	802	1154	1391	0.173	0.182	0.187	438
ZnO:Pb (15%)	714	938	1370	0.170	0.177	0.187	438
ZnO:Pb (20%)	638	878	1190	0.167	0.175	0.183	438

of lead which indicates presence of shallow trapping states at higher concentrations of Pb in host ZnO. Table 1 shows the values of the trap-depths for different concentration of dopants. The trap-depth value has been found to be maximum (0.189 eV) in case of ZnO:Pb (5%) nanophosphor sample, while it is minimum (0.167 eV) for ZnO:Pb (20%). The emission wavelength is found to be 438 nm for each sample. We observed no change in the emission wavelengths of the nanophosphor samples on increasing/decreasing the concentration of the dopants in host ZnO

Conclusions

High purity nanobelts of ZnO having lengths in the range of several hundreds of micrometers to a few millimeters have been synthesized in the laboratory. Intersting results are obtained from SEM studies of the synthesized nanobelts. Length of the nanobelts varies from a few micrometers to a few millimeters. SEM studies confirm the wurtzite crystal structure and high crystallanity. The decrease in the life time value is observed with the increase in the concentration of impurity. ZnO nanobelts have several applications and can be employed as best suited materials for white LED, gas sensors, better insulation materials, high energy density batteries etc. It is concluded that at higher concentrations of Pb doping in host ZnO phosphor has more emission intensity by several orders of magnitude and life-time shortening indicate that these nanobelts are having fast decay times as compared with low dopant concentrations.

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