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Enhanced optical properties La doped ZnO nanoparticles

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Rare earth metal Lanthanum doped ZnO nanoparticles are synthesized by using hydrothermal method. The products are characterized by X-Ray powder Diffraction, Scanning Electron Microscopy and Transmission Electron Microscopy. The optical properties of the product are studied. Luminescence property is enhanced for the doped ZnO nanoparticles

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1. Introduction

Synthesize and study of nanostructured materials have become a major attractive interdisciplinary area of research over the past fast few decades. Recently, transition metal(TM) and rare earth ion doped II-IV semiconductor nanoparticles have received much attention because such doping can modify and improve optical properties of II-IV semiconductor nanoparticles by large amount [1-5]. Usually, semiconducting nanoparticles are known to exhibit exotic physico-chemical properties due to quantum confinement effect. Especially, doped luminescent nanoparticles are predicted to show improved optical properties, viz., luminescence efficiency, and delay time and band edge emission with respect to particle size variation. These properties have opened up a number of new areas of applications for these materials such as DNA markers, biosensors, light emitting diodes, lasers, etc as well as in spintronics and photocatalyst. Different routes to obtain doped ZnO materials have been studied [6] namely, the incorporation of rare earth metal ions into a semiconductor photocatalyst by ion implantation or by co-precipitation. Doping with rare earth elements leads to many interesting properties of ZnO. In this article, it is reported that the synthesis of La doped ZnO nanoparticles rheological phase reaction-precursor method and characterization of the sample by XRD, SEM and TEM analysis. UV absorption and PL spectroscopy has been used to study the influence of La doping on the optical properties of ZnO nanocrystals at room temperature.

2. Methods and materials

ZnO, $Zn_{1-x}La_xO$ (x=0, 0.01, 0.03) was synthesized by a rheological phase reaction-precursor method. Stoichiometric quantities of the raw materials viz. Zinc acetate (Zn $(CH_3COO)_2$)(ZA), Lanthanum acetate $(La(CH_3COO)_3).4H_2O$, (LA)and Oxalic acid $(H_2C_2O_4.2H_2O)$ were used as precursors. The reaction between 0.1M solution of Zinc Acetate and 0.15M solution of oxalic acid gave maximum amount of intermediate product as compared to the other ratios of precursors. [7]. Initially, 0.1M of ZA and yM (y=0.001, 0.002, 0.003) of LA were stirred in 100ml water until the solution becomes transparent. Lanthanum and Zn oxalate were prepared by slow addition of oxalic acid with stirring for 12 hours at room temperature. The precipitate was filtered and cleaned with acetone several times to remove impurities, dried at 120 ° C for 5 hours and ZnO and $Zn_{1-x}La_xO$ nanoparticles were obtained thermal decomposition of the oxalates at 450 °C for 2h in air. The powdered samples were characterized by powder X-ray diffractometer XPERT PRO with $Cuk_\alpha X$ ray radiation (λ=0.15496 nm). The surface morphology of the samples is observed by Scanning Electron Microscopy (SEM, JEOL, JSM-67001). Optical Absorption spectra are taken with SHIMDZU UV-310PC, UV scanning spectro-photometer. The room temperature photoluminescence (PL) spectra of ZnO and doped ZnO nanoparticles are recorded with fluorescence spectrometer (FLS920) using Xe lamp as the excitation source at excitation wavelength (λ_{ex} = 325 nm).

3. Results and discussion

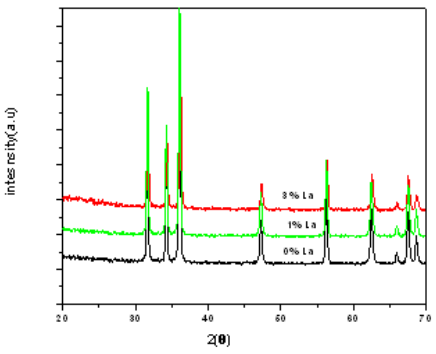

Fig. 1. (a) X ray Diffraction pattern of ZnO nanoparticles for various concentration of La.

The crystal structure of pure and La doped ZnO nanomaterials were characterized using XRD. Fig. 1 shows a typical XRD spectrum for the $Zn_{1-x}La_xO$ (x=0,0.01,0.03) calcined at 450 C in air. There are slight shift of XRD peaks to higher angle for the doped ZnO samples, no difference in XRD patterns was found in the samples. For each sample, all the observed diffraction peaks can be indexed to a wurtzite structure as ZnO (space

group $P6_3mc$, JCPDF#36-1451) and no secondary phase were found. The particle sizes of the products for the different dopant concentrations were tabulated in Table 1, which is calculated from X-ray line broadening using the Scherer formula D=kl/b half-maximum line width, and l is the wavelength of the X-rays.

Table 1. Size of the particle determined from XRD.

Doping concentration	FWHM (deg)	Particle Size (XRD) nm
0%	.26	29
1%	.34	25
3%	.40	20

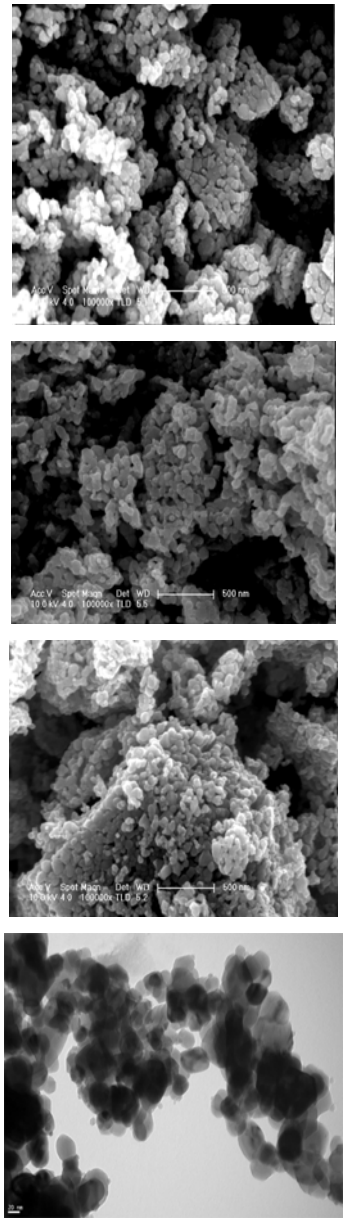

Fig. 3. (a), (b),(c), SEM images for 0%,1%, 3% La doped ZnO and (d)TEM image of 3% La doped ZnO.

Fig. 3(a-c) shows the SEM images of pure and La doped ZnO nanocrystals for different concentrations. The uniformly distributed hexagonal shaped particles were observed for the doped ZnO nanocrystals. The particle sizes decrease for doped ZnO nanocrystals. Fig. 3d is a typical TEM image of the 3% La doped ZnO sample.

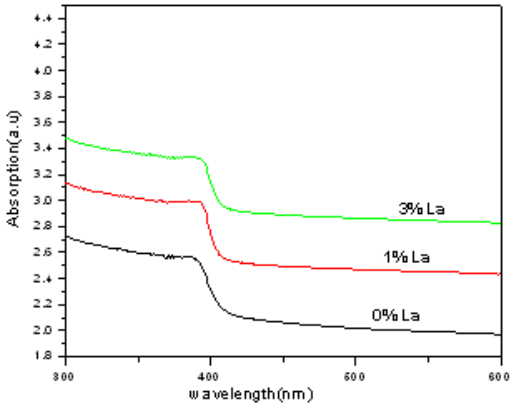

Fig. 4. (a) UV absorption spectra of ZnO for various La concentration.

Substitution of La cations in tetrahedral sites of the wurtzite structure was confirmed by UV-vis optical spectroscopy. The room temperature spectra of the pure and doped ZnO nanoparticles are reported in Fig. 4(a). From the spectrum the band edge is shifted to the shorter wavelength side of the La doped ZnO samples as compared to the pure ZnO sample. The blue shift in the absorption spectrum edge is a clear indication for the incorporation of La inside the ZnO lattice [8,9].

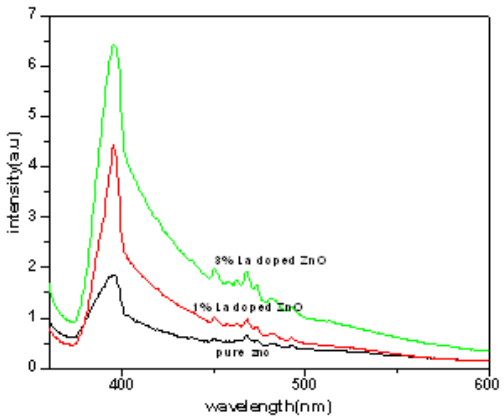

Fig. 4. (b) PL spectra of ZnO nanoparticles for various La concentration.

Fig. 4(b) Shows photoluminescence (PL) for pure and doped ZnO nanocrystals for different concentrations. We observed luminescence peak at 390 nm. There is substantial enhancement of luminescence intensity due to the increase of La concentration. La ions act as effective luminescent centers. The PL results show that the doped

rare earth elements are the major luminescent component and can effectively improve the luminescence of ZnO: La nanoparticles

4. Conclusion

La doped ZnO nanocrystals were successfully synthesized by hydrothermal method and they are characterized by XRD, SEM and TEM analysis. The optical properties of as prepared samples were investigated by UV and PL analysis. The La doped ZnO crystals exhibited higher luminescence activity than a pure ZnO nanocrystals Enhanced photoluminescence activity suggests that these La doped ZnO nanoparticles will find many interesting applications in semiconductor photocatalysis, solar cells and nanodevices.

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