



Synthesis and comparative study of Ho and Y doped ZnO nanoparticles

Shubra Singh*, J.N. Divya Deepthi, B. Ramachandran, M.S. Ramachandra Rao

Department of Physics, Materials Science Research Centre and Nano Functional Materials Technology Centre, Indian Institute of Technology (IIT) Madras, Chennai-600 036, India

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ABSTRACT

Ho and Y doped ZnO nanoparticles were synthesized using a wet chemical route followed by structural, electrical and magnetic property characterization of the same. We present a comparison of the properties of Ho and Y (having same ionic radii) doped ZnO nanoparticles. X-ray diffraction studies of the diffraction data exhibit a monophasic wurtzite crystal structure similar to that of the parent compound, ZnO. Microstructural investigations of these samples by scanning electron microscopy show the presence of nanostructures. The optical measurements show an increase in the band gap of doped samples as compared to the undoped sample. DC magnetization measurements of Ho doped ZnO point towards the presence of hysteresis loop at 5 K with an H_c of about 110 Oe for a nominal 1 mol% Ho doped sample. The resistivity of Ho doped sample is found to be higher as compared to the undoped and Y doped sample.

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1. Introduction

ZnO based diluted magnetic semiconductors (DMSs) offer the possibility of probing magnetic phenomena in crystals with a simple band structure and excellent magneto-optical and transport properties. Doping transition metal ions into ZnO as well as other wide band gap oxides and III–V semiconductors has been shown to propagate carrier-induced ferromagnetism [1,2]. It is notable that Coey et al. [3] proposed donor impurity band exchange in DMS oxides, showing that shallow donor electrons mediated ferromagnetic exchanges. However, there has been no unanimous agreement on the experimental results on transition-metal-doped ZnO. Recent results on Gd doped GaN, indicating high magnetic moments [4] have motivated us to investigate ZnO samples doped with rare earth (RE) metal ions. For the 3d transition metals, the 3d electrons are exterior and delocalized; leading to strong direct exchange interactions and high Curie temperatures, but often the orbital momentum is zero, leading to small total magnetic moments per atom. In the case of RE doping, the 4f electrons are localized; exchange interactions are indirect as they occur via the 5d or 6s conduction electrons. However the high orbital momentum leads to high total magnetic moment per atom. Glasses and crystals doped with rare-earth (RE) metal ions are still attractive as a possible active media for solid state lasers, operating in the visible, near-infrared (NIR) and infrared (IR) spectral region. RE doped ZnO also have potential applications as visible light emitting phosphors in high power lasers and other optoelectronic devices [5,6]. Detailed

literature survey shows that there are not enough reports on the systematic studies of rare earth ions like Ho doping in ZnO. With this motivation, Ho was doped into ZnO matrix by sol–gel method and investigated to understand the optical, electrical and magnetic properties of the Ho ion doped samples. These properties have also been compared with Y doped ZnO nanoparticles (having nearly the same ionic radii as that of Ho), however, the difference being that Ho is magnetic ($\mu_{\text{eff}} = 10.4 \mu_B$) and Y is nonmagnetic.

2. Experimental

Doped ZnO nanoparticles were synthesized by sol–gel route (more information on synthesis given in supplementary information). The composition of the samples was determined by energy dispersive X-ray analysis. The phase purity and crystal structure of the samples were analyzed by PAN analytical Xpert-Pro-PHILIPS using $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5405 \text{ \AA}$). Sample characterization was carried out using high resolution scanning electron microscopy (HRSEM-PHILIPS, QUANTA-200), high resolution transmission electron microscopy (HRTEM), diffuse reflectance spectroscopy or DRS (Ocean optics USB 2000 spectrophotometer) respectively, Vibrating sample Magnetometer (VSM) and Impedance analyzer (Agilent 4294A, USA).

3. Results and discussion

Powder X-ray diffractograms of the compounds (Supplementary Fig. 1), obtained using a $\text{Cu-K}\alpha$ radiation show single phase formation. In all these cases the data fitted well to the wurtzite and it is clear that these samples were of polycrystalline nature without any secondary phases. All the peaks in both Ho and Y-doped ZnO samples could be

* Corresponding author. Tel.: +91 44 22575912.
E-mail address: shubra6@gmail.com (S. Singh).

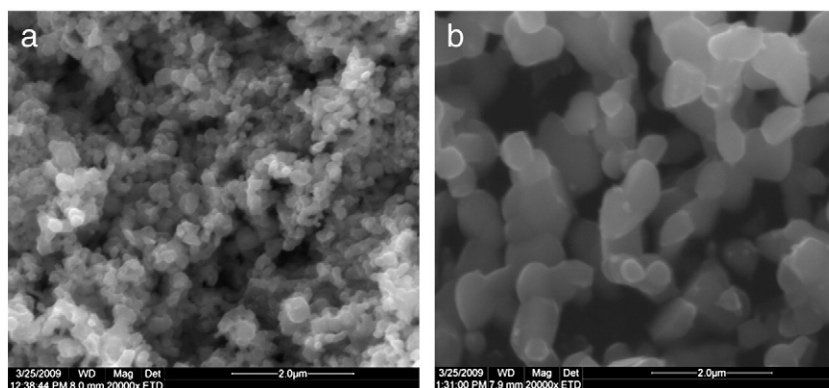


Fig. 1. HRSEM images of (a) Ho and (b) Y doped ZnO samples.

fitted with wurtzite structure (space group $P63mc$ (No. 186)). Slightly enlarged lattice parameter values were obtained for Ho and Y-doped samples (1 mol% Ho-doped ZnO, $a = 3.254(1) \text{ \AA}$, $c = 5.209(2) \text{ \AA}$, and 1 mol% Y-doped ZnO, $a = 3.253(2) \text{ \AA}$, $c = 5.211(2) \text{ \AA}$) in comparison with that of undoped ZnO sample ($a = 3.248(1) \text{ \AA}$, $c = 5.200(2) \text{ \AA}$) prepared under identical conditions. It was seen that, both as-prepared doped samples have broad XRD peaks due to their nanocrystalline nature. The shift in the peak position towards higher angle side and the decrease in the c -axis length can be attributed to the tensile stress and structural defects that is introduced in the host lattice upon Ho and Y ion doping [7]. It was also noted that the FWHM increases implying decrease in the crystalline quality. The area energy dispersive X-ray analysis (EDAX) (Supplementary Fig. 2) also revealed excellent homogeneity of the samples and is in good agreement with the nominal starting compositions. EDAX analysis carried out on 1 mol% doped ZnO samples showed that the concentrations of Ho and Y in ZnO were nearly 0.94 mol% and 0.82 mol% respectively, consistent with the low level of doping. Figs. 1 and 2 present the HRSEM and HRTEM images of Ho and Y doped ZnO nanoparticles respectively. It is evident from the images that the diameter of Ho doped ZnO nanoparticles are smaller than the Y doped samples and lie within 70–100 nm as compared to Y doped nanoparticles which are ~150–200 nm in size. Though the doping percentage was same (1 mol%), the size of nanoparticles in the two samples was found to be different. The clear lattice stripes in the inset of Fig. 2(b) show that it is crystalline in nature with the interplanar distances of 0.26 nm, which corresponds to that of the (001) plane of wurtzite ZnO. The corresponding Fourier Fast Transformation (FFT) pattern characterizes further the wurtzite structure.

DRS of homogenized powder samples was recorded by collecting scattered light from powdered samples (using a BaSO_4 powder

compact as a reference sample). DRS on the as prepared samples show a blueshift in band gap edge of both Ho and Y doped samples. The decrease in particle size of Ho doped samples led to an increase in the band gap by 18 meV (Fig. 3(a)) as compared to the bulk undoped compound. In order to study the influence of Ho and Y doping on the optical properties of the samples, photoluminescence (PL) measurements have been carried out. PL spectra (not shown here) were recorded using He–Cd laser (325 nm) as the light source for optical pumping. PL spectra of Ho doped ZnO sample have been found to display broad bands in previous studies, which have been attributed to ZnO intrinsic self activated centers. The structures obtained in these spectra correspond to the reabsorption of emitted light by the dopant. For Y, no such structure has been found. In case of our samples no characteristic emission based on emission center of rare earth metals was observed for the Ho and Y doped ZnO doped samples. These results suggest that the emission centers existing as the rare earth metals are not excited by photo excitation, and energy transfer does not occur from the ZnO to the dopants. However, the PL emission shows a blue shift in the excitonic spectra (reflecting an increase in band gap) due to the decrease in particle size of doped samples, thus corroborating the DRS measurements on the samples.

Electrical measurements of doped samples indicate that the resistivity of Ho and Y doped samples is $\sim 10^5$ and $10^4 \Omega\text{-cm}$ respectively. Thus the samples can be regarded as insulating. It is interesting to see that the Ho-doped compounds have more resistivity compared to the Y-doped compounds, although Ho and Y ions have almost the same ionic radii and hence lattice strain effect would be the same in both the cases. The nearly equal ionic radii ($Y_{i,r} = 1.018 \text{ \AA}$; $Ho_{i,r} = 1.015 \text{ \AA}$) of the two substituted elements negate the effect of internal strain [8] (as the tolerance factor t is the same for both the cases) on the observed magnetic and electric properties. These results

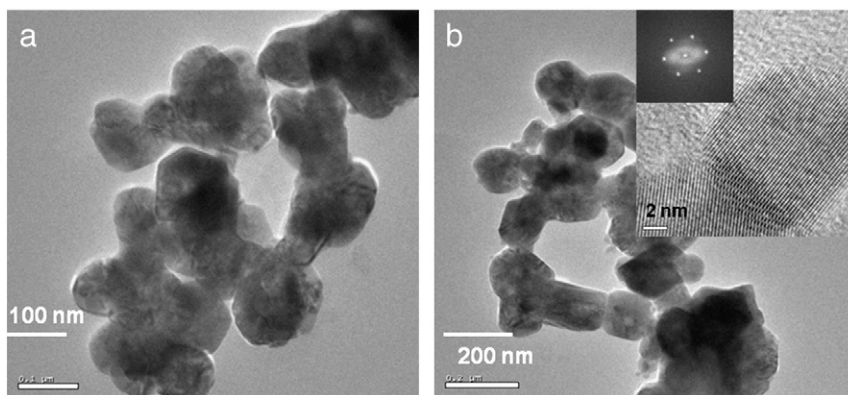


Fig. 2. HRTEM images of Ho and Y doped ZnO samples. Inset shows the fast fourier transform (FFT) pattern of magnified image.

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