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Influence of Co doping on the structural, optical and magnetic properties of ZnO nanocrystals

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ABSTRACT

A systematic investigation on the synthesis, characterization, optical and magnetic properties of Co doped ZnO nanocrystals have been reported. Nanocrystals of $Zn_{1-x}Co_xO$ (where $x = 0.05$ and 0.10) were synthesized using the Sol–gel technique. Structural, optical and magnetic properties of the samples were investigated by X-ray diffraction (XRD), UV–VIS–NIR spectroscopy, Raman spectroscopy and SQUID magnetometer. Energy dispersive X-ray, Scanning electron microscopic, XRD and Raman measurements showed that the Co ions were successfully doped at the Zn site in the wurtzite type ZnO lattice. An appreciable blue shift in the absorption spectrum was observed, which indicates that the Co doping in ZnO leads to systematic increase in the band-gap with dopant concentration. Magnetization studies showed that the Co doped ZnO nanocrystals display room temperature ferromagnetism and the ferromagnetic ordering strengthens with the Co concentration.

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1. Introduction

The room temperature ferromagnetism (RTFM) in dilute magnetic semiconductors (DMS), have stimulated enormous research interest due to their potential use in new spin based devices (spintronics). In the spintronics devices there is a possibility to utilize both charge and spin degree of freedom, which results in the design and fabrication of new generation of microelectronic devices like as spin-valve transistor spin light emitting diodes, optical isolator, and ultra fast optical switches, etc. These new devices inspired researchers to conduct extensive research work on the synthesis of doped and un-doped diluted magnetic semiconductor (DMS) in various forms, shapes and sizes and investigation of their physical properties [1,2]. In recent years special attentions have been paid to the wide band-gap dilute semiconductor such as ZnO, GaAs, In_2O_3, TiO_2 and GaN because when doped with transition metals, they do show ferromagnetism at room temperature [3,4]. Among these DMS systems maximum attentions have been paid to ZnO due to its unique opto-electronic properties (direct bandgap of 3.3 eV and large exciton binding energy 60 MeV) and its use in many applications such as in light emitting diodes, photodetectors and gas sensors [5].

Introduction of impurity ions into the ZnO host matrix is a magic and effective method to develop novel functionalities into ZnO. For example dilute doping of 3d transition metal ions (e.g., Mn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+}) incorporation into the nonmagnetic ZnO system can introduce ferromagnetic functionalities while its semiconducting properties can be retained [6,7]. Amongst transition metals Mn and Co have been found to be the most promising elements for tailoring the optical and magnetic properties of ZnO based DMS. Dietl et al. [8] have reported theoretically that ZnO based DMS should exhibit RTFM when doped with different 3d transition metal (TM = Co, Mn, Fe, Ni, Cr, etc.).

The experimental results regarding RTFM in Co doped ZnO systems in the form of thin films, bulk, polycrystalline and nanocrystalline samples, however, differs widely with the optical and magnetic properties of such compounds depends upon the synthesis method employed. Rode et al. [9] have reported the intrinsic ferromagnetic behavior of Co doped ZnO films with their T_c higher than 300 K. $Zn_{1-x}Co_xO$ films prepared using sol–gel methods have been also found to display RTFM [10], although secondary phases have been present in the samples $x \geqslant 0.25$. Some group have observed RTFM in the absence of secondary phase of Cobalt clusters [11,12] and others also reported absence of ferromagnetism [13]. Singhal et al. have reported $Zn_{1-x}Co_xO$ ($x = 0.0$–0.07) nanocrystals

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to be ferromagnetic at room temperature. They have detected donor defects bound to Co site by Raman spectroscopy and shown that the activation of RTFM depends on defects, such as oxygen vacancies and Zn interstitials [14].

Study on Co-doped ZnO nanorods fabricated by a facile solution route, Hao et al. have reported red-shift in the wavelength of the absorption edge and room temperature ferromagnetism in low doped sample, which is greatly suppressed and replaced by paramagnetism at higher doping levels [15]. In a very recent study on the Co-doped ZnO nanorods prepared by hydrothermal method, Shi et al. have reported that these samples undergo a change from FM to PM with doping concentration increasing, where the ferromagnetic behavior can be attributed to defect-mediated Co^{2+}–Co^{2+} coupling in a ferromagnetic way [16]. It is worth to mention that most of the studies in Co doped samples were carried out at ~5% Co doping level. Recently Mohapatra et al. had established that 5% Co doping in ZnO is the optimal doping level [17].

The above discussion suggests that the origin and general understanding of RTFM in doped and un-doped ZnO is not yet fully resolved and under debate, even though large numbers of experimental studies have been reported and numbers of theories have been proposed. Less attention has been paid to sample with Co concentration exceeding 5%. Hence, it is of prime importance to keep researching the optical and magnetic properties of the doped and un-doped ZnO based systems in various forms, shapes and sizes.

Thus, it is worth to synthesize Co (up to 10%) doped ZnO sample using sol–gel method and study the structural, optical and magnetic properties. In this article, we report a systematic study on the structural, optical and magnetic properties of Co doped ZnO nanocrystals. The samples have been synthesized using the sol–gel method and their detailed structural characterization has been made with the help of XRD, EDX, and SEM studies. UV–VIS–NIR and SQUID magnetometer methods have been employed to study the optical and magnetic properties. Raman spectroscopic measurements have been also done to find the role of TM–O vibrations and oxygen vacancies on the RTFM.

2. Experimental details

Three nanocrystalline samples in the series $Zn_{1-x}Co_xO$ (with $x = 0$, 0.05, 0.1) were synthesized using the standard sol–gel procedure. Zinc acetates (Zn $(CH_3COO)_2H_2O$) and Cobalt acetates (Co $(CH_3COO)_2H_2O$) were taken as the starting precursors. Initially an appropriate amount of Zinc and Cobalt acetates was dissolved in N,N-dimethylformamide (DMF) by constant stirring at room temperature for each composition. Resulting sols were evaporated in a heating mental and finally the dried precursors were collected.

The single phase purity and crystalline structure of the nanocrystalline samples were determined by powder X-ray diffraction. Diffraction patterns were collected on a Bruker D8 Advance X-ray diffractometer using Cu Kα as an X-ray source. The scans were taken in the 2θ range from 20° to 90° with a step size of 0.01°. Rietveld profile refinements of the XRD patterns were carried out using the FULLPROF Program. Elemental analyses of the samples were done with the help of energy dispersive X-ray (EDX) measurements. The morphology of the samples was analyzed using scanning electron microscopy (SEM).

Structure of all the Co doped ZnO nanocrystalline samples were also investigated by Raman spectroscopy. In Raman spectroscopy incident photons interact with the molecules and the amount of energy change of phonon characteristic of the nature of each bond (vibration) present. The Raman measurements were performed on a DeltaNu Advantages series 532 with a Charge coupled device (CCD) detector and a Green laser (operated at 532 nm) as an exciting light source. The Charge coupled devices (CCD) makes the Raman spectroscopy technique millions of times more sensitive than the eye and a complete Raman spectrum can be recorded in less than a second. In order to eliminate heating effects the output power of laser was kept at 100 mW with 10 s integration time for every samples.

Optical absorption spectra were recorded on a Perkin–Elmer Lambda 750 UV–VIS–NIR spectrophotometer with pre-aligned Tungsten, Halogen and Deuterium sources. The resolution of the spectrophotometer is 0.17–5.00 nm for UV–VIS and 0.20–20.00 nm for NIR. Temperature and field dependent dc magnetization measurements of the samples were done on a MPMS XL7 make Superconducting Quantum Interference Device (SQUID). The MPMS XL7 consists of several superconducting parts which are magnets to generate large magnetic fields, a detection coil coupling inductively to the sample, a SQUID sensor connected to the detection coil and a magnetic shield surrounding the SQUID. The magnetization of the samples was recorded in the temperature range from 5 to 300 K and in external magnetic field of up to ±5.0 T.

3. Results

3.1. Characterization and crystal structure

3.1.1. XRD patterns

Fig. 1a–c shows the fitted XRD patterns of pure and Co doped (5% and 10%) ZnO samples i.e. the $Zn_{0.95}Co_{0.05}O$ and $Zn_{0.90}Co_{0.10}O$ recorded at 300 K. All the Bragg peaks in these diffraction patterns can be indexed in the ZnS type Wurtzite hexagonal symmetry and no detectable peak from any other phase have been observed. The pure ZnO and $Zn_{0.90}Co_{0.10}O$ are single phase samples with no signature of any extra peak from any other impurity phase. However, in the diffraction pattern of $Zn_{0.95}Co_{0.05}O$ few minor reflections at low angles can be observed. Rietveld profile refinement of the XRD patterns have been carried out in the $P6_3mc$ space group (No. 186, $Z = 3$), with each atom in the Wurtzite hexagonal structure residing on the 2b Wyckoff position with the Zn atoms at (1/3, 2/3, 0) and the O atoms at (1/3, 2/3, z) co-ordinates. The analysis shows that Co atoms are well incorporated into the ZnO lattice and occupy the Zn site with total preference. The results of the analysis have been listed in Table 1. The obtained cell parameters for ZnO are in very good agreement with the reported values. The estimated values of lattice parameters for all the Co doped ZnO samples have been found to be very close to those of undoped ZnO and the atomic positional parameters have been found quite close to those reported for the parent compound ZnO. There is no appreciable change in the unit cell volumes, which is obviously a consequence of the quite closer ionic size of Co^{2+}(0.58 Å) and Zn^{2+}(0.60 Å).

Fig. 1d displays the X-ray diffraction patterns of pure and Co doped ZnO nanocrystalline samples, in a limited range, displaying only the three major Bragg reflections. It can be clearly seen that the peak widths in doped samples get broadens due to the formation of smaller average crystallites as a result of increase in disorder on Co^{2+}. Interestingly, the relative intensity of these major XRD peaks varied with the Co concentration. These observations indicate the nanocrystalline nature of the doped samples. The average grain size (D) of the crystallite was estimated with the help of Debye–Scherrer formula,

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where k is the particle shape factor (0.9), λ is wave length of Cu Kα radiation (1.5406 Å), β is the full width at half maxima (FWHM) of XRD peak and θ is the diffraction angle of the peak. The estimated average crystallite sizes were found to be 95 nm and 115 nm for 5% and 10% Co doped samples, respectively.

3.1.2. EDX and SEM measurements

The elemental percentage of Co in the doped ZnO samples has been obtained with the help of energy dispersive X-ray (EDX) analysis. The EDX data showed that the amount of Co incorporated in the ZnO matrix is less than that the initial concentration of Co ions. Fig. 2 depicts the EDX spectra of 10% Co-doped ZnO. The spectra reveal that only three elements, Zn, Co and O exist in the sample and the amount of Co is found to be 7.72 at atomic weight percentage.

The morphologies of all the samples have also been analyzed using scanning electron microscopy (SEM). The SEM micrographs of the three samples pure and Co doped ZnO nanocrystals as synthesized are shown in Fig. 3a and b, respectively. The micrographs have clearly showed random shaped nanocrystals of the samples with wide size distributions.

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