Optical and magnetic properties of Yb ion-doped cobalt-based ZnO nanoparticles for DMS applications

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Abstract. Well-crystalline structured ZnO nanoparticles with cobalt (Co) and ytterbium (Yb) multiple ions doping were successfully synthesized by the chemical precipitation technique. The structures, optical and magnetic properties of the samples were analysed with X-ray diffraction (XRD), UV–visible spectroscopy and magnetic measurements, respectively. In the XRD pattern of the pure ZnO and Yb co-doped samples, the formation of highly crystalline phase of pure ZnO was observed even at high Yb concentration. UV–vis spectra show a strong UV absorbance for all the samples with different absorbance maxima. Magnetic characterizations have shown that the sample with 1% Yb co-doped ZnO:Co nanoparticles exhibited a clear ferromagnetic (FM) behaviour at room temperature. The X-ray photoelectron spectral peaks for Yb 4f ions reveal Yb occupation of both Yb³⁺ as well as Yb²⁺ states. Hence, it can be confirmed that a clear FM behaviour at room temperature was exhibited by an imbalanced valence state of Yb that strongly interacted with the Co²⁺. When compared to the Co-doped ZnO, Yb co-doped ZnO exhibits a clear ferromagnetism at room temperature with high coercivity due to the contribution of both 3d and 4f exchange interaction with the host matrix.

Keywords. Chemical synthesis; rare earth metals; co-doping; ferromagnetism.

1. Introduction

Dilute magnetic semiconductors (DMSs) have been one of the most interesting materials due to their potential application towards the spintronics, where the charge and spin of electrons is used simultaneously for the data processing in spin-based information storage and optical devices.¹ The main challenge of the DMS's applications is to attain a ferromagnetic (FM) property at room temperature (RT).² The ZnO-based semiconductors have been demonstrated as an ideal DMS material due to high solubility of transition metals (TMs), good semiconducting properties, wide bandgap (3.27 eV) and large exciton binding energy (60 meV) compared to the various materials such as Mn-doped GaAs and Mn-doped GaN.³ ZnO doped with many TMs by DMSs was investigated, Mn,^{4,5} Co,^{6–9} Ni,^{2,10} Fe^{11–13} and Cu,^{2,14} and reported to have the high Curie temperature that is above RT. The local magnetic moment in doped TM ions leads to sp–d exchange interaction that induces ferromagnetism at high temperature. However, it remains under debate whether the room temperature ferromagnetism (RTFM)

in TM-doped ZnO semiconductors is due to the intrinsic or extrinsic origin.¹⁵ On the other hand, some reports suggested that RTFM in ZnO is a intrinsic FM origin which may be due to oxygen deficiency, cation vacancy and defects in the crystal structure.^{15–17} Banerjee *et al*¹⁸ reported that the enhancement of ferromagnetism in pure ZnO powder upon thermal annealing was linked to the formation of oxygen vacancy (V_O). Xu *et al*¹⁹ also reported ferromagnetism in ZnO thin films and attributed it to the intrinsic defects. Till date, the researchers have controversial issue with this observed ferromagnetism in DMS, which is due to magnetic impurities or intrinsic nature of the material.² To overcome this, the various research groups are finding the versatile DMS material for spintronics and other magneto-optical device fabrication.

In case of Co-doped ZnO-based DMS, till date there is no clear concept about the nature and origin of magnetic properties. Some reports suggested that the presence of the double exchange interaction in Co clusters is the reason for the origin of ferromagnetism in Zn_{1–x}Co_xO.⁷ In contrast, in recent times the absence of ferromagnetism in Co-doped ZnO nanoparticles were reported by Duan *et al*²⁰ and Rao–Deepak.²¹ Hence the exact origin of ferromagnetism in magnetic Co²⁺ ion-doped ZnO-based

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DMSs is controversial and still in serious discussion. However, it is believed that the presence of additional carrier introduced by co-doping can enhance the ferromagnetism in ZnO:Co²⁺. In past decades, the effect of co-doping on RTFM in GaN doped with the rare earth (RE) element Gd was reported. Hite *et al*²² reported the effect of Si co-doping on the electrical and magnetic properties of GaN:Gd and found four times increase in saturation magnetization (M_s). Zhou *et al*²³ reported an approximately seven times enhancement in GaN:Gd magnetization by Si co-doping. Only few reports have been published with additional carrier-doped ZnO-based DMSs. Also aggregation in ZnO:Co lattice affects the magnetic interaction in ZnO DMS. The effect due to aggregation can be controlled by the co-doping and growth technique.²⁴

In recent times, the RE-doped ZnO semiconductors are an active research area. In RE metal-doped oxide semiconductors, the 4f electrons in RE ion are localized and directed the exchange interactions via 5d or 6s conduction electrons, which offer high total magnetic moments per atom because of their high orbital momentum.^{25,26} Therefore, unlike the d states, f electrons can couple strongly with the host s electrons, leading to the possibility of electron-mediated ferromagnetism in these materials.^{27,28} Earlier results show that RE doping process in the semiconductor host material plays an important role to obtain interesting optical and magnetic properties because of its efficient energy transfer property that is used in magneto-optical device.²⁹ On the other hand, the 4f RE dopants like Eu, Pr and Gd have been widely investigated due to their high magnetic moments, excellent fluorescence properties and high stability. Therefore, it can be considered as an alternative to 3d TMs to induce the RTFM.²⁴

Moreover, RE ions have special electronic structure which may be favourable for desired luminescent features; especially, their valence electrons located in 4f orbit surrounded by filled 5s and 5p orbits. Due to the effective shielding by both 5s and 5p orbits, the environment impact on 4f electron's transition is limited.³ Therefore the exact ferromagnetism without the inclusion of other interactions is measured. Consequently, the RE metal ions have very stable optical transition, many energy levels, many metastable states and a very good fluorescence in the UV and visible region, which is needed for desired luminescent features. Based on previous reports, obtaining good optical and magnetic properties from the nanomaterials is fully based on the doping of selective elements only. Among various RE ions, Yb is one of the interesting elements which exhibit unique optical features with their partially filled f electron states. In the electronic configuration of Yb³⁺, the 4f electron is less shielded than other RE ions which makes a high interaction with host lattice and shows the excellent sensitizer for TM ions. Also recent reports are confirmed that

Yb³⁺-doped laser material is a promising diode pumped laser medium.³⁰

In this present study, for the first time the RTFM in chemically precipitated Co with Yb co-doped ZnO nanoparticles is discussed. In addition, their structural, optical and morphological features are also investigated. The aim of this study is the enhancement of luminescence properties and magnetic properties of the ZnO nanoparticles by co-doping with dual impurities (i.e., one is nonmagnetic (Yb) and the other is magnetic material (Co)). The main challenge for this kind of materials is to attain their magnetic character at RT and good optical property in order to be useful for magneto-optical device applications.

2. Experimental

2.1 Synthesis process

The analytical grade, zinc nitrate tetrahydrate, cobalt nitrate tetrahydrate and ytterbium nitrate hexahydrate were used as starting materials. The materials were obtained from Merck (Germany ~99.9%), and used without further purification. The typical synthesis process is as follows: the stoichiometric amount of the above-mentioned starting materials were dissolved in 20 ml of deionized (DI) water separately under stirring. The Yb concentrations are fixed as 1, 3 and 5% with the 10% constant cobalt concentration. The precursor solutions were rapidly mixed together to form a homogeneous mixture. After that, 1 M of NaOH solution was added dropwise to the above mixture over 20 min at RT. Immediately, Zn(OH)₂ was formed as white precipitate. The stirring was continued for 2 h and aged for 12 h to complete the nucleation process. Finally, the precipitate was washed with DI water, ethanol, and acetone consecutively through centrifugation to remove the possible ions remaining in the final product. The end product was dried and calcined at 300°C for 3 h. For comparison, pure ZnO nanoparticle was also synthesized by following the same procedure without the addition of Co and Yb ions. For easy identification, the prepared samples were named as Z (pure ZnO), ZC (cobalt-doped ZnO), ZCY1 (1% Yb doped with cobalt and ZnO), ZCY3 (3% Yb doped with cobalt and ZnO) and ZCY5 (5% Yb doped with cobalt and ZnO).

2.2 Characterization

The crystalline structure was evaluated by X-ray diffraction (XRD) using PAN analytical instrument, using CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) with the scanning rate of $0.05^\circ \text{ s}^{-1}$ in the 2θ range from 20° to 80° . Fourier transform infrared (FTIR) spectra were observed with Perkin Elmer infrared spectrophotometer. Morphology and microstructure were identified by high-resolution scanning electron microscope (HRSEM, Quanta 200 FEG

~5 kV) equipped with energy-dispersive X-ray (EDX) analysis and transmission electron microscope (TEM Philips Model: CM-20), respectively. UV-vis spectra of the nanoparticles were obtained using (Shimadzu UV-2450) UV-vis-NIR spectrophotometer. Photoluminescence (PL) spectra were recorded using a He-Cd laser source with an excitation wavelength of 325 nm by Perkin Elmer L45 fluorescence spectrophotometer at RT. X-ray photoelectron spectra (XPS) were recorded using an AlK α ($h\nu = 1486.6$ eV) used as X-ray source by sigma probe (Thermo Scientific). Magnetic studies of the prepared samples were carried out on vibrating sample magnetometer (Lakeshore VSM 7410) at RT.

3. Results and discussion

3.1 Structural study

XRD pattern of pure and Co with Yb co-doped ZnO nanoparticles is shown in figure 1. It is evident that diffraction peaks of all the samples can be indexed to the hexagonal wurtzite structure of ZnO. Only the diffraction lines of the wurtzite ZnO were observed without any other peaks in Co-doped ZnO and Yb co-doped (even up to 5% of Yb) nanoparticles.³¹ It clearly indicates that the Co and the Yb ions are successfully incorporated into the ZnO lattice site. Compared to pure ZnO, the doped samples show the low intensity and increased full-width half-maxima in XRD patterns. In detail, the peak (101) of Co-doped ZnO nanoparticles shows a slight shift towards higher angle $\sim 0.11^\circ$ which has good agreement with previous report.³² Whereas the Yb co-doped sample shows that the peak (101) shift towards the lower angle due to the additional strain induced by the co-dopant in ZnO

lattices.^{29,33} The shift towards the lower angle illustrates that Yb³⁺ ions with larger ionic radius (1.01 Å) have been successfully incorporated into the ZnO lattice and substituted the Zn²⁺ ionic sites (0.74 Å).³⁴ The average particle size of pure and Co-doped ZnO nanoparticles are calculated with the maximum intensity peak (101) by using the Scherrer equation. It is found to be in the range of 25–19 nm for ZnO : Co with Yb doping nanoparticles.

3.2 Morphological studies

Figure 2a–f represents the SEM images of pure (a and b), Co-doped ZnO (c and d) and 1% Yb co-doped ZnO (e and f) nanoparticles. Figure 2a and b shows the undefined aggregated morphology of the pure ZnO nanoparticles. By adding Co into ZnO the morphology has been converted to flake-like structure (figure 2c and d). There is no significant change observed in the surface morphology with the addition of Yb. Captured SEM images of the Yb co-doped ZnO nanoparticles clearly show that the self-assembled nanoflakes appeared with coarse morphology. With the addition of Yb into ZnO, the typical nanoflakes are self-assembled together and try to form the flower-like morphology as can be seen in figure 2e and f. This result indicates that the addition of Yb varies the surface energy and connects the nanoflakes together forming the flower-like microstructure for 1% Yb co-doped ZnO. The significant variation in the grain size was observed by the addition of Yb, which may be due to the interaction of Yb and Zn lattice. The EDX spectra for Co with 1% Yb co-doped ZnO nanoparticles are shown in figure 3a–c. The peak intensities in the spectra are consistent with appropriate concentrations of atoms present and assured the existence of Zn, Co, Yb and O without any impurities. To further confirmation, TEM analysis was taken for 1 mol% of Yb-doped ZnO nanoparticles which are shown in figure 4a–d. TEM images indicate the formation of nanoflake microstructure of the compound with coarse morphology. The observed TEM photographs confirm that coarse frame of nanoparticles assembled together and formed nanoflakes.

3.3 Optical studies

The UV-vis absorption spectra were used to find possible changes in electronic structure.¹⁸ The UV-vis absorption spectra of pure and Co with Yb co-doped ZnO nanoparticles are shown in figure 5a. The spectrum of pure ZnO has strong UV emission peak at 358 nm. The UV emissions are commonly due to the reason of direct recombination of free excitons of ZnO.²⁹ After being doped with Co and Yb, the absorption peaks shifted towards higher wavelength region from 358 to 363 nm, i.e., red shifted with the increase in the Yb concentrations.³⁵ The Yb³⁺ ions introduce the electronic state impurity energy band

Figure 1. XRD patterns of pure and Co with Yb co-doped ZnO nanoparticles.

Figure 2. Scanning electron micrographs of (a and b) pure ZnO, (c and d) Co-doped ZnO and (e and f) 1% Yb co-doped ZnO : Co nanoparticles.

Table 1. Atomic concentration of elements for pure and Co:Yb co-doped ZnO nanocrystals measured from the EDS analysis.

Compound name	Atomic % of Zn	Atomic % of Co	Atomic % of Yb	Atomic % of O
Z	59.73	—	—	39.74
ZC	50.15	9. 81	—	40.04
ZCY1	49.23	9.41	0.97	40.37

Figure 3. (a–c) Energy-dispersive X-ray spectra of pure and Co with Yb co-doped ZnO nanoparticles.

into the energy band of ZnO which are very close to the conduction band. This introduction of impurity band gives rise to the reduction in bandgap and red shift in UV region.³⁵ Bandgap was measured with Tauc's plot by using the Mott and Davis relation $\alpha h\nu \sim (h\nu - E_g)^{1/2}$ for allowed direct transitions as reported earlier. From figure 5b, energy bandgap E_g for Co with Yb co-doped ZnO nanoparticles is found to be in the range of 3.25–3.15 eV. Bandgap value for co-doped Yb^{3+} decreases when compared to pure and Co-doped samples. As a result, the electronic structure of ZnO nanoparticles can be tuned when Yb^{3+} ion is doped into ZnO lattice which may give the good optical properties for the doped samples.³⁶

3.4 PL studies

PL spectra of the Yb co-doped ZnO:Co nanoparticles are shown in figure 6a and b. A strong UV–visible emission band for the corresponding UV excitation of 325 nm is observed. The pure ZnO shows the characteristic emission band at 382.6 nm followed by the deep-level visible emission and it can be observed for all the samples. The UV emission arises from the recombination of

exciton–exciton through collision process.²⁹ Besides, a strong and broad green emission band at around 550 nm was observed in pure ZnO. This deep-level visible band is commonly due to the intrinsic defects like oxygen vacancy and zinc interstitials.³⁷ After the addition of Co (10%), both the characteristic and deep-level emission intensity decreases due to the low intrinsic optical behaviour of the Co ions. This confirms the partial substitution of Co into Zn site that makes the changes in the crystal structure which is consistent with morphological studies. The Yb co-doped ZnO nanoparticles show the significant changes in the PL spectra as shown in figure 6b. Compared with the PL spectrum of pure ZnO, UV emission of Yb-doped ZnO nanoparticles exhibits smaller blue shift and the green emission band is sharply suppressed. For RE-doped ZnO nanoparticles, more electrons are contributed by dopants which would take up the energy levels located at the bottom of the conduction band. When they were excited by the laser of 325 nm, the excitons take up higher-energy levels at the bottom of the conduction band and radioactive recombination of these excitons leads to a blue shift.³⁸ This blue shift of UV emission reveals the incorporation of Yb ions on Zn lattice sites which supports the X-ray studies.³⁶ With increasing of Yb

Figure 4. (a–d) TEM images of ZnO : Co doped with 1% Yb nanoparticles.

Figure 5. (a) UV–vis absorption spectra of pure and Co with Yb co-doped ZnO nanoparticles and (b) bandgap spectra of pure and Co with Yb co-doped ZnO nanoparticles.

concentration, the blue emission has been observed in the PL spectra with the increase in intensity. This arises from the doped Yb ions that introduced a new impurity level into energy bandgap of ZnO, which leads to different transitions and gives blue emission.³⁹ Based on previous

literatures, the enhanced intensity of the blue emission confirms that the increased density of defects, which could be attributed to the defect introduced by the existence of Yb impurities in ZnO nanoparticles.^{36,39,40} Also the occurrence of blue emission at 440 nm is associated

Figure 6. PL spectra of (a) pure and Co-doped ZnO nanoparticles and (b) Co with Yb co-doped ZnO nanoparticles.

with defect centres present below the conduction band of ZnO nanoparticles. This confirms the influences of Yb in luminescent behaviour of ZnO nanoparticles by introducing additional energy transitions within the ZnO lattices. The observed enhanced blue emission on PL spectra confirms that the Yb^{3+} ions are successfully substituted into ZnO lattice. Moreover, the fact that the intensity of Yb-PL is comparable or higher than that of ZnO which indicates that the transfer from ZnO to Yb^{3+} ions can be quite efficient.⁴⁰ Also the enhancement of UV-emission may be due to the following reasons: (i) ZnO lattice consists of a singly ionized oxygen vacancies which may be affected by the Yb^{3+} doping, (ii) creation of more electron-hole pairs with Yb^{3+} doping and (iii) energy transfer process from Yb^{3+} ions to ZnO.^{34,40} This result of UV-vis absorption spectra is consistent with earlier reports.

3.5 Magnetic studies

DMSs based on the RE:ZnO exhibit larger magnetic moments due to their strong FM coupling between f-electron of RE ions and s-electrons in host semiconductor.²⁵ Furthermore, the origin of ferromagnetism in RE-doped semiconductors is not yet confirmed because of the controversial reports. It is well demonstrated that the presence of f-electrons in appropriate concentration can enhance the FM coupling in the RE diluted semiconductor oxides.²⁸ However, the results do not convince the scientists. Therefore, it is important to realize the FM features of RE-doped semiconductors.

RT hysteresis curve for Co- and Yb-doped ZnO nanoparticles is shown in figure 7a and b. It can be seen that pure ZnO nanoparticles show only paramagnetism.

Doped ZnO with Co alone exhibits weak ferromagnetism without clear saturation as shown in figure 7a (red). The different concentrations of Yb added ZnO:Co, nanoparticles show a significant variation in the $M-H$ curve. Noticeably, 1% Yb-doped ZnO:Co nanoparticles exhibit RT ferromagnetism, which corresponds to the FM coupling between s-electrons of the Co and 4f-electron of Yb ions via ZnO.^{28,41,42} It is mainly attributed to 1% Yb which provides sufficient electron density to FM coupling and results in the well-established $M-H$ curve as shown in figure 7b. The origin of ferromagnetism may be due to the exchange interactions between localized electron spin moments, resulting from oxygen vacancies or defects in the ZnO samples.⁴³ It is believed that the addition of Yb makes great influence on the hexagonal ZnO nanostructure by means of creating the Zn vacancy as well as Co clustering. This leads to the observed RTFM. Further increase in the Yb concentration to 5 mol%, the paramagnetic contribution is dominated, due to large number of localized 4f electrons in Yb ions. Unlike 3d TM ions, in this case of mixed 3d and 4f electrons coupling occur indirectly via 5d or 6s conduction electrons via host material.²⁹ In addition, the presence of Yb^{3+} states may also directly influence the new exchange mechanism through intra-ion and inter-ion coupling, thus inducing ferromagnetism.

3.6 XPS analysis

XPS analysis was carried out for the sample 1%-Yb-doped Co:ZnO nanoparticle to further confirm the observed FM behaviour of both 3d (Co) and 4f (Yb) ion-doped ZnO nanoparticles. Typical XPS spectra of the

Figure 7. (a) Magnetization hysteresis ($M-H$) curves of pure (inset), Co-doped (ZC), and Co with Yb co-doped (ZCY3 and ZCY5) ZnO nanoparticles and (b) magnetization hysteresis ($M-H$) curves of 1% Yb with Co-doped ZnO (ZCY1) nanoparticles.

Figure 8. (a–d) XPS spectra of Co with 1% Yb Co-doped ZnO nanoparticles.

sample are illustrated in figure 8a–d. The XPS spectrum of Co 2p as shown in figure 8b indicates the well-resolved Co^{2+} energy peaks at 780.06 and 795.54 eV with the satellite peak at ~ 790 eV. The energy difference between Co 2p_{3/2} and Co 2p_{1/2} is 15 eV, which matches with that of standard CoO and confirms the presence of Co^{2+} in ZnO lattices.⁴⁴ The Yb-4d peak in figure 8c reveals that two peaks with binding energies of 159 and 165 eV are identified as Yb 4d_{3/2} and Yb 4d_{5/2}, respectively. These findings suggest the presence of Zn and Yb in the doped ZnO nanoparticles in the form of Zn 2p and Yb 3p oxidation state.^{34,45} Hence, it can be confirmed that the imbalanced valence state of Yb has strongly interacted with the Co^{2+} , thereby inducing RTFM. From the XPS spectra of Zn 2p and O 1s as shown in figure 8a and d, it is further understandable that ZnO can be highly desirable host semiconductor to make a facile dilute magnetic semiconductors. The strong XPS peaks at 1022.37 and 1045.33 eV due to Zn 2p electron evidence the dominant ZnO phase that has been formed even after the 5% of Yb doping in addition to the Co. The two peaks situated at about 530.7 and 531.3 eV, respectively, corresponding to the binding energy of Zn–O bonds in bulk ZnO. The broad peak at 531.3 eV may be related to the O^{2-} ions in the oxygen-deficient regions within the ZnO matrix, which indicates a good co-ordination between metal and oxygen.⁴⁰ There is no additional peak found in the XPS survey spectrum due to impurities, which further confirms the phase stability of the semiconductor. From this investigation it can be concluded that the simultaneous doping of Co and Yb into ZnO increases the electron density and hole density in the host matrix. Here Yb^{3+} leads to the exchange interaction with Co through ZnO and thus facilitates the induced ferromagnetism.

4. Conclusion

In summary, the synthesis of pure ZnO nanoparticle with Co and Yb co-doping by the simple chemical precipitation method for dilute magnetic semiconductor applications is reported. The structure and optical features of the prepared samples are confirmed with XRD and photoluminescent analysis. As expected, 1% Yb co-doped ZnO:Co nanoparticle exhibits ferromagnetism at RT. The observed ferromagnetism arises due to the combined exchange interaction between 3d electron in Co^{2+} and delocalized 4f electron in Yb with the host. In particular, the occupation of Yb^{3+} state varies the hole and electron density with the ZnO system. It also favours the inter- and intra-band exchange interaction via ZnO. Hence it induces the interesting low-field ferromagnetism in Yb co-doped ZnO nanoparticles. We conclude that Yb introduces the charge imbalance in ZnO with sufficient electron density at 1% Yb co-doping, resulting in an exhibition of clear ferromagnetism at RT.

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