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Ferromagnetic property of ZnO: Co^{2+}:Bi^{3+} Nanocrystals for DMS applications

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Abstract: Well crystalline Co-Bi codoped ZnO nanostructures with various concentration of Bi were synthesized by simple chemical precipitation technique using metal nitrate precursors. The structural and magnetic properties of the samples calcined at 300 °C for 6 h has been studied comprehensively. X-ray diffraction patterns (XRD) of the pure and Co-with Bi doped samples have shown the well crystalline diffraction peaks corresponds to the characteristic wurtzite ZnO crystal structure. Excellent ferromagnetic features of the material at room temperature reveal the additional carrier induced exchange interaction could enhance the ferromagnetism in co-doped ZnO nanostructure. The addition of Bi at 3^+ states can act as donor within the semiconductor which provides the additional electron charge carrier that could involve directly to the exchange interaction effectively at certain limit and enhances the ferromagnetism.
Key words: ZnO nanocrystals; optical materials; energy band gap; dilute magnetic semiconductors.

Introduction and Experimental Techniques:

Room temperature ferromagnetism (RTFM) in dilute magnetic semiconductors (DMS) has received much attention owing to their potential application in electron spin based electronic devices [1-3]. One among from the various materials, ZnO doped with transition metals has been extensively investigated for DMS applications [2&4]. Till date the researchers have argued with this observed ferromagnetism in DMS, which is either risen from the magnetic impurities and intrinsic defects in semiconductor crystals or intrinsic nature of the material [2].Many similar and controversial reports have been published earlier with RTFM and their absence in various pure and magnetically diluted semiconductors [5].The occurrence of RTFM in DMS system may be due to the following reasons; cation vacancy, oxygen deficiency and defects in their crystal structure [6]. Many reports were found that the different metal ions such as Mn [7], doped ZnO facilitates for RTFM. In this study, it is reported that the room temperature ferromagnetism in chemically precipitated ZnO:Co:Bi nano particles by tuning the concentration of co-dopant (Bi^{3+}) systematically with the fixed magnetic ion (Co^{2+}).

The Analytical grade, Zinc nitrate tetra hydrate, cobalt nitrate tetra hydrate and bismuth nitrate hexa-hydrate were used for precursor sources. Above precursor sources were dissolved in 20 ml of deionized water

separately under stirring. The typical Co and Bi concentrations are 10% and Bi concentration varied from 1-4% respectively. 1 M of NaOH solution was added. The stirring was continued to 2 h and aged for 12 h.

Results and Discussions:

Phase Analysis

XRD pattern of as prepared pure and Co with Bi co-doped ZnO nanoparticles were shown in Fig 1(a). Well defined diffraction peaks have been directly indexed to hexagonal phase wurtzite crystal structure. On contrary to Co doped ZnO pattern, the Bi co-doped shows the lower angle shift in the diffraction peaks corresponds to the strain induced by the co-dopant. At higher concentration of Bi (above 2%), the Bi_2O_3 secondary phase were formed with negligible intensity.

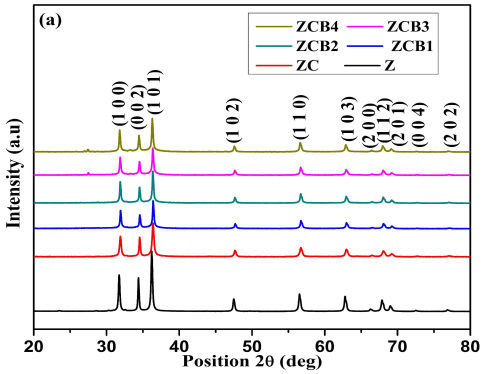

Fig.1(a) XRD patterns of pure and Co with Bi co-doped ZnO nano particles

Magnetic Studies

Figure 2(a) shows that the Magnetization versus applied magnetic field (M-H) curves of chemically precipitated pure (inset), Co-doped (ZC) and Bi co-doped ZnO (ZCB2-ZCB4) nanoparticles. As expected, the pure ZnO (Fig 2(a) inset) shows paramagnetic nature without any hysteresis loop. By adding the 10% cobalt, ferromagnetic ordering was observed in room temperature at low field region This is due to the Co^{2+} doping induced exchange mechanism in ZnO host and which is consistent with earlier reports. Especially, 1% Bi with Co doped ZnO (ZCB1) shows anomalous ferromagnetic features and is shown in Fig (2b). Further by increasing Bi^{3+} content it can be seen that significant deduction in hysteresis loop and diamagnetic transition were observed. In contrast, the electronic configuration of Bi^{3+} is [Xe] $4f^{14}5d^{10}6s^2$ has localized lone pair electron in their outermost s-orbital. Due to this, ferromagnetic interaction with semiconductor is not possible because Bi intrinsically exhibits diamagnetic spin ordering in nature. We believe that Bi addition 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 room temperature ferromagnetism. Alternatively, the only possibility for the occurrence of anomalous ferromagnetism in Bi-Co doped ZnO by the way to the carrier mediated exchange interactions. This associates to Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interaction [8]. In this study, we suggest a similar kind of exchange mechanism may be originating the anomalous ferromagnetic features in Bi co-doped Co:ZnO nanoparticles.

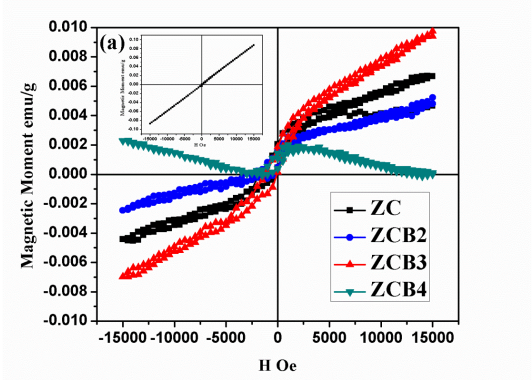

Fig. 2(a) Magnetization hysteresis (M-H) curves of pure (inset), Co-doped (ZC) and Co with Bi co doped (ZCB2, ZCB3 and ZCB4) ZnO nanoparticles

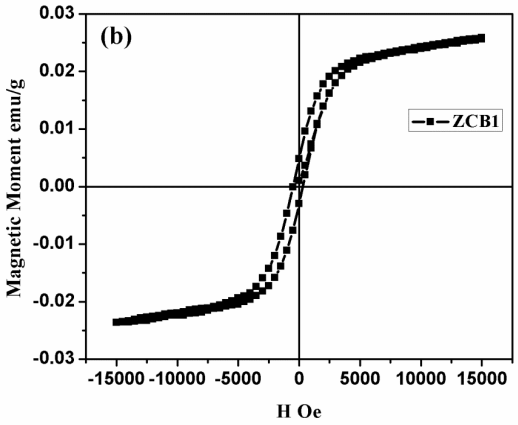

Fig. 2(b) Magnetization hysteresis (M-H) curves of Co with Bi-1% co-doped ZnO nano particles.

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