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Photoluminescence and Raman studies for the confirmation of oxygen vacancies to induce ferromagnetism in Fe doped Mn:ZnO compound

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ABSTRACT

With a motivation to compare the magnetic property, we synthesised undoped, transition metal (TM) Mn doped and (Mn:Fe) co-doped ZnO ceramics in the compositions ZnO, $Zn_{0.98}Mn_{0.02}O$ and $Zn_{0.96}(Mn_{0.02}Fe_{0.02})O$. Systematic investigations on the structural, microstructural, defect structure and magnetic properties of the samples were performed. Low temperature as well as room temperature ferromagnetism has been observed for all our samples, however, enhanced magnetisation at room temperature has been noticed when ZnO is co-doped with Fe along with Mn. Particularly the sample with the composition $Zn_{0.96}Mn_{0.02}Fe_{0.02}O$ showed a magnetisation value more than double of the sample with composition $Zn_{0.98}Mn_{0.02}O$, indicating long range strong interaction between the magnetic impurities leading to higher ferromagnetic ordering. Raman and PL studies reveal presence of higher defects in form of oxygen vacancy clusters created in the sample due to Fe co doping. PL study also reveals enhanced luminescence efficiency in the co doped sample. Temperature dependent magnetisation study of this sample shows the spin freezing temperature around 39 K indicating the presence of small impurity phase of $Mn_{2-x}Zn_xO_3$ type. Electron Spin Resonance signal obtained supports ferromagnetic state in the co doped sample. Enhancement of magnetisation is attributed to interactions mediated by magnetic impurities through large number of oxygen vacancies created by Fe^{3+} ions forming bound magnetic polarons (BMP) and facilitating long range ferromagnetic ordering in the co- doped system.

1. Introduction

Transition from paramagnetism (PM) to ferromagnetism (FM) in magnetic semiconductors is a prominent topic in condensed matter physics because of efforts to discover materials useful for spintronics applications. This is recently an active area of research as spin-based multifunctional electronic devices have several advantages over the conventional charge-based devices regarding data-processing speed, nonvolatility, higher integration densities, etc. [1]. The impending need to obtain such devices has led to the growing interest in developing magnetic semiconducting materials essential for use as spin injectors; yet single phase materials with a Curie temperature T_c well above 300 K compatible with today's technologies have not been identified. Controlling and tuning the magnetic properties in diluted magnetic oxide semiconductor (DMS) like ZnO, SnO_2 and TiO_2 by exploiting the charge and spin degrees of freedom of electrons simultaneously, are of current interest of research for potential memory device applications [2,3]. However, problems encountered so far in the efforts to increase the transition temperature T_c in these wide band gap semiconductors suggest that a deeper understanding on the system is highly essential.

Transition metals (TM) that have partially filled d states (unpaired electrons) with electronic configurations like Fe ($4s^23d^6$), Co ($4s^23d^7$) and Mn ($4s^23d^5$); have been extensively used as magnetic impurities in DMSs for spintronics based devices. 3d orbitals of the transition metal ions are hybridised with p orbitals of the cations of the host semiconductor, which magnetically couples the localised 3d spins of magnetic ions with the spin of charge carriers in the host semiconductors. However, in spite of the wide variety of experimental reports, some controversies are still associated regarding the explanation towards the nature and origin of ferromagnetic ordering in TM doped dilute magnetic

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oxide systems [4,5]. Some researchers proposed spin-split donor impurity band model, where the long range ferromagnetic exchange can be mediated by polaronic percolation of bound magnetic polarons (BMP) formed via defects like oxygen vacancies, which is an entity, consisting of a charge carrier bound to an ionised impurity and encompassing magnetic ions with locally aligned spins [6]. The defect induced shallow donor levels gets hybridised with the TM d-band and thus stabilizes ferromagnetic ground state in diluted samples, where there is no possibility of nearest neighbour interaction. Although the BMP model does not entail a high carrier density, it does require high-density spin polarised impurities which mediate the exchange interactions. Some other opinions are for long-range ferromagnetic coupling by the hybridisation picture of super-exchange, double-exchange and spinodal decomposed phase supported magnetic network predicted by Monte-Carlo simulation; resulting in a high-T_c phase.

As known, ZnO has been known to be an excellent host matrix for doping with magnetic TM ions. Experimentally, among all TM impurities; Mn is widely used for doping into ZnO, owing to its similar radius (0.083 nm) with Zn atom (0.074 nm) and high solubility. But, the outcomes of experimental results in Mn-doped ZnO are controversial and obtaining room temperature ferromagnetism and its origin are still quite debated [7]. On the other hand, for Fe doped ZnO, difficulty to get high T_c due to low solubility of Fe in ZnO and a phase separation; easy to form clusters or a secondary phase of $ZnFe_2O_4$ for a dopant concentration >2 at% has been quite disappointing [5,8].

Taking into account of all the mentioned facts, an effective route to achieve enhanced ferromagnetism and raise the Curie temperature could be to adopt co doping with two different 3d TM impurities into ZnO, instead of a single. It was proposed that the ferromagnetism can be attributed to the mediation of vacancies. However, it is hard to control the concentration of vacancies as well as the density of carriers in the doped system. Fortunately, the density of carriers and defect states can be mediated effectively in these co doped systems giving rise to long-range magnetic order. Explanation toward the ferromagnetic behaviour is given in terms of bound magnetic polarons and carrier-mediated exchange [6,9] respectively. Meanwhile, several co doped ZnO systems have also been reported [10–12] successfully so far, where co doping with shallow acceptors and donors has been used to adjust the carrier density of the system such that it can switch from the diluted magnetic insulator (DMI) to DMS behaviour. In fact, authors have also reported (Mn:Ni) co- doped ZnO system with improved magnetic property [13]. Since Fe is popular as a contributor of higher individual magnetic moment, co doping with Fe would be an equally interesting issue to be addressed. Moreover, it has been found that chemically Fe can be co doped in ZnO effectively along with Mn and Co [14–16] for higher ferromagnetism ($\sim 10^{-2}$ emu/g).

Motivated by the above theoretical and experimental observations, we have synthesised (Mn:Fe) co doped ZnO samples. Here we report, an increase in the saturation magnetisation up to more than twice that of Mn doped ZnO, in (Mn,Fe) co doped ZnO sample prepared by solid state sintering technique and sintered at low temperature. Possibilities of the presence of impurity phases and exchange interactions due to Fe co doping in Mn:ZnO were explored through different characterisation techniques. Effort has been made to explain the origin and stability of ferromagnetic behaviour and ensure the reliability and reproducibility as well.

2. Experimental

Appropriate proportion of high pure oxides of Zn, Mn and Fe (Purаterm-99.999%) were used for the synthesis of ZnO, $Zn_{0.98}Mn_{0.02}O$ and $Zn_{0.96}Mn_{0.02}Fe_{0.02}O$ pellets by usual solid state reaction technique mentioned elsewhere [17]. Pellets prepared from above compositions were sintered at 500 °C for 8 h by slow step sintering route using a high temperature programmable (Eurotherm controller, Model: 2404) vacuum furnace. X-ray diffraction (XRD) and scanning electron microscopy studies were carried out by Bruker D8 Advance X-ray diffractometer and SEM (Philips FEG Xl'30), respectively for structural and morphological analyses. Micro-Raman studies were carried out with Horibo Raman Microscopy, France, laser 514 nm, power 100 mW, to analyse the structural change as well as examine the presence of defects in the system after doping and co doping. To have more information on the defect structure, PL measurement was performed by Fluorolog-3 spectro-flourometer attached with a 450 W xenon lamp, using 350 nm excitation. Magnetic measurements of the samples were recorded at room temperatures (300 K) using superconducting quantum interference device (SQUID) magnetometer with maximum field of 10,000 Oe. Electron Spin Resonance (ESR) signals were obtained by using a Bruker EMX Plus system.

3. Result and discussions

XRD patterns of the three samples of ZnO, Mn doped ZnO ($Zn_{0.98}Mn_{0.02}O$) and (Mn:Fe) co doped ZnO ($Zn_{0.96}Mn_{0.02}Fe_{0.02}O$) are presented in Fig. 1. All the peaks in the doped and co doped samples could be indexed to the wurzite structure of ZnO, indicating no structural change due to doping of Mn and Fe in ZnO. No sign of extra peaks corresponding to any impurity, cluster or secondary phase found within the XRD detection limit also signifies the single phase of the doped systems and incorporation of the dopants into the lattice sites in host ZnO. In Fig. 1, it is worth noticing that the higher intensified peak (101) has been shifted towards lower 2θ value in the Mn doped ZnO sample as expected, whereas for the (Mn:Fe) co doped sample there has been a clear shift towards the higher 2θ value. This is due to the replacement of Zn^{2+} ions of radius 0.74 nm by the bigger Mn^{2+} ions of radius 0.83 nm in the Mn doped sample and by Fe^{3+} ions of radius 0.64 nm in the (Mn:Fe) co doped sample. The lattice parameters calculated from XRD analysis; shows that for Mn doped samples there is an increase, whereas for the (Mn:Fe) co doped sample, a decrease as compared to the undoped ZnO sample. However, the c/a ratio remains unchanged after doping and co doping reveals

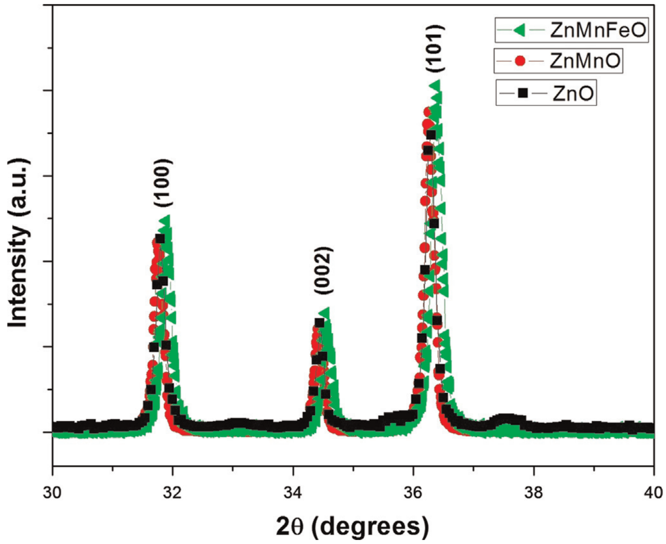

Fig. 1. XRD patterns of ZnO, Mn doped ZnO and (Mn:Fe) co doped ZnO samples.