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Significant enhancement of room temperature ferromagnetism in surfactant coated polycrystalline Mn doped ZnO particles

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Abstract

We report a surfactant assisted synthesis of Mn doped ZnO polycrystalline samples showing robust room temperature ferromagnetism as characterized by X-ray diffraction analysis, transmission electron microscopy, electron paramagnetic resonance and DC magnetization measurements. This surfactant assisted synthesis method, developed by us, is found to be highly reproducible. Further, it can also be extended to the synthesis of other transition metal doped ZnO.

Keywords: Mn doped ZnO; Dilute magnetic semiconductor oxide materials; X-ray diffraction; Transmission electron microscopy; DC magnetization measurements; Surfactant assisted synthesis

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1. Introduction

There is extensive interest in the growth of wide band gap oxide semiconductors, which are ferromagnetic at room temperature. In particular, Mn doped ZnO has attracted substantial interest [1,2]. Despite clear theoretical predictions [3,4], ferromagnetism in Mn doped ZnO remains poorly understood experimentally. Often different laboratories have reported incongruous results for seemingly identical materials. Several authors have observed only paramagnetism at any temperature [5,6], while others have reported ferromagnetism with T_c below room temperature [7]. Sharma et al. [8] was the first to report room temperature ferromagnetism in thin films by PLD, and bulk powders of Mn doped ZnO, produced by low temperature solid state reaction. They have attributed the observed ferromagnetism to carrier induced, from a theoretical study. Later, Kundaliya et al. [9] claimed the origin of room temperature ferromagnetism (RTF) to arise from a totally different compound (Zn doped Mn_2O_3) and not from Mn substituting for Zn in the ZnO wurtzite structure. However, any doubt about the intrinsic nature of ferromagnetism in Mn doped ZnO was cleared by the more recent work of Kittilstved et al. [10]. They have demonstrated the reversible cycling of paramagnetic (P) to ferromagnetic (RTF) state in Mn doped ZnO nanocrystals by chemical manipulation. However, the situation in the case of bulk materials is still not clear. Hong et al. [11], in a recent paper, highlighted the role of defects in tuning ferromagnetism in oxide DMS films. In view of this, we thought it is worth while to explore ways to fine tune synthesis conditions to optimize magnetic characteristics of Mn doped ZnO bulk samples. In this communication, we present our efforts in fine tuning preparation conditions for optimizing ferromagnetic characteristics of Mn doped ZnO bulk samples reliably by surfactant treatment and calcinations, in a reproducible way.

2. Experimental

The procedure involved heating a mixture of AOT (sodium bis(2-ethylhexyl) sulfosuccinate) or triblock co-polymer (poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)) (Pluronic 123) and the bulk samples of Mn doped ZnO (prepared by the method followed by Sharma et al. [8]) at 400 °C for 1 h, followed by washing and drying of the samples. Dried powders were calcined at 400 °C for 4 h in air. Mn doped ZnO with different Mn concentrations were prepared by standard solid state reaction route [8], using high purity ZnO (99.999%, May & Baker Ltd., Dagenham, UK) and MnO_2 (99.9999%, Spex Ind. Inc., NJ, USA) powders. Appropriate amounts of ZnO and MnO_2 powders were mixed, calcined at 400 °C for 8 h and sintered in air at 450 °C for 12 h and cooled to room temperature normally to obtain nominal $Zn_{1-x}Mn_xO$ ($x = 0.0, 0.01, 0.022, 0.03, 0.04$, and 0.05) powders. These samples

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were then mixed with AOT (sample to AOT weight ratio 1:10), heated at 400 °C for 1 h and subsequently washed using distilled water and absolute ethanol several times and dried at 125 °C for 16 h. This dried powder is annealed at 400 °C for 4 h in air. The mixing of AOT and Mn doped ZnO sample is accomplished by weighing the required quantity of AOT and making a hollow ball out of it. Then the weighed Mn doped sample is put into the AOT ball. The AOT ball containing the doped sample is then placed in an alumina boat and heated in a tubular furnace at the rate of 10 °C/min, at 400 °C as mentioned above). Phase purity and the structure of the samples were analyzed using Cu Kα radiation by employing a Philips Diffractometer (model PW 1071) fitted with graphite crystal monochromater. The lattice parameters of the compounds were extracted by Rietveld refinement of the XRD data by using the program Fullprof [12] with X-ray intensity collected for the range $10° \leq 2\theta \leq 70°$. DC magnetization measurements as a function of field were carried out using an E.G. &G P.A.R vibrating sample magnetometer (model 4500). Electron diffraction and microscopy were carried out with a JEOL, JEM 2010 transmission electron microscope (TEM) for morphological and high-resolution electron microscopy (HREM) studies. Specimens were prepared for TEM by placing a drop of the suspended particles on carbon-coated Cu grids. The EPR experiments were performed using BRUKER ESP 300 spectrometer operated at X-band frequency (9.5 GHz). DPPH was used for calibrating the g values.

3. Results and discussion

Rietveld Profile refinement analysis of XRD data of $Zn_{1-x}Mn_xO$ ($x = 0.0$, 0.01, 0.022, 0.03, 0.04, and 0.05) showed that they are single phase with the wurtzite structure (space group $P6_3mc$). The dependence of cell volume with dopant concentration is presented in Fig. 1. The linear increase of cell volume with dopant concentration indicates the incorporation of Mn into ZnO lattice [13,14]. Since X-ray diffraction analysis being a bulk technique, one cannot detect inclusions of minute secondary phases. In order to make sure the samples are free from secondary phases, we have carried out transmission electron microscopic analysis on 2.2 at.% Mn doped ZnO treated with AOT.

The bright field images of the particles of sample corresponding to 2.2 at.% Mn doped ZnO show narrow distribution in shape and size, with particles exhibiting predominantly rod-like microstructure developing into platelets and sizes in the range of 50–200 nm as depicted in Fig. 2a. The particles are uniformly coated with the surfactant layer (thickness of coating ∼1 nm, more clearly seen in Fig. 2c). The particles are highly crystalline, homogenous, and devoid of any small clusters or secondary phases as has been thoroughly investigated by scanning large portions of the particles on the grid. The selected area electron diffraction (SAED) pattern of one such particle taken with $B = [2\text{-}1\text{-}10]$ is shown in Fig. 2b. Electron diffraction pattern shows that the particle exhibit monocrystalline wurtzite ZnO structure. The high resolution electron micrograph in Fig. 2c shows the lattice fringe width of ∼2.8 Å, corresponding to (01-10) plane of wurtzite ZnO phase.

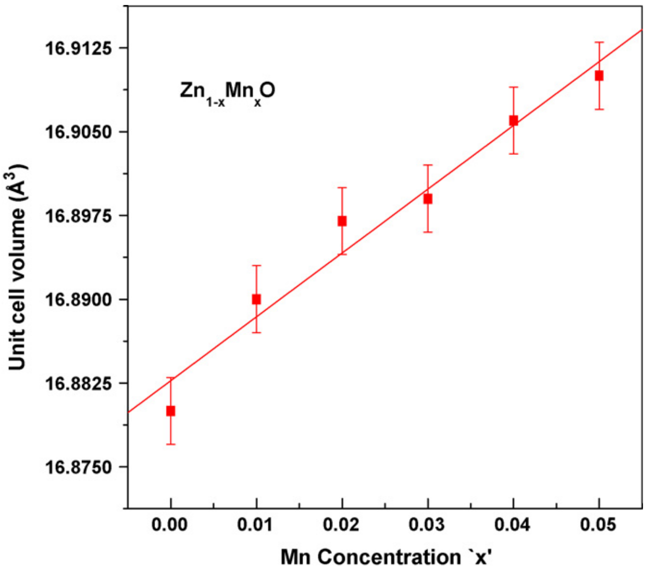

Fig. 1. Cell volume dependence on dopant concentration ‘x’ in $Zn_{1-x}Mn_xO$.

DC magnetization loops of Mn doped ZnO without AOT is given in Fig. 3. From this figure it is clear that the increase in Mn concentration decreases the ferromagnetic nature and increases the paramagnetic component of samples in agreement with the results of Sharma et al. [8]. Fig. 4 shows the M–H curves of the same samples after AOT treatment followed by calcination at 400 °C. It can be seen that the magnetic moment of all samples, in particular 2.2 at.% Mn doped ZnO, increases significantly after AOT treatment followed by 400 °C calcinations. For 2.2 at.% Mn doped ZnO, the saturation magnetization (Ms) is 0.05 emu/g with a coercieve field (Hc) of 125 Oe (Fig. 5, inset) and remanence (Mr) of 0.008 emu/g. This value of Ms is about seven times the value (0.007 emu/g) obtained by Sharma et al. [8] for 2.2 at.% Mn doped ZnO, and about five times the value (0.01 emu/g) of our 2.2% Mn doped as synthesized sample. The decrease of ferromagnetic nature of samples with increase in Mn concentration beyond 2.2 at.% Mn may be due to the clustering as a consequence of decreased Mn–Mn distance leading to antiferromagnetic nearest neighbour exchanges [8]. Sharma et al. [8] observed maximum ferromagnetic moment for their 2.2 at.% Mn doped ZnO and found that the ferromagnetic nature decreases with increase in Mn concentration. In our case also, we have observed maximum ferromagnetic moment for 2.2 at.% Mn doped sample and so we have given more emphasize to this particular sample. To see the effect of different surfactants on the magnetic properties, we treated the sample 2.2 at.% Mn doped ZnO using tri block co-polymer (Pluronic 123) instead of AOT. The results are presented in Fig. 5. It can be seen that the AOT coated sample shows almost 100% enhancement in saturation magnetization value as compared to co-polymer treated sample. These experiments, for all Mn compositions, were repeated several times using both AOT and co-polymer and have been found to be highly reproducible.

Fig. 6 shows the EPR spectra recorded at room temperature on 2.2 at.% Mn doped ZnO with and without AOT coating. EPR spectrum of 2.2 at.% Mn doped samples clearly showed two signals one at low field corresponding to the FMR signal [8,15,17,18] which arises from transition within the ground state of ferromagnetic domain, and the other due to the well known EPR spectrum (sextet hyperfine structure) [16] of Mn^{2+} ions which may not be participating in the ferromagnetic ordering. It can be seen from the EPR spectrum (Fig. 6) that for sample, which is not treated with AOT, the signal corresponding to Mn^{2+} ions is more intense than that treated with AOT. Fur-