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Structural and magnetic property of Mn:ZnO bulk ceramic doped with rare earth (Gd/Sm) atoms

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ABSTRACT

This paper reports the paramagnetic behavior of Mn doped ZnO co-doped with rare earth (Gd and Sm) atoms. The formation of secondary rare earth oxides (Gd_2O_3 and Sm_2O_3) is confirmed from the X-ray diffraction patterns. The rare earth oxides in the system forbids the grain growth and interconnection between the grains. The weak link between the grains suppresses the long range exchange interaction between the Mn ions and hence, reduces the ferromagnetic ordering. Owing to the large mismatch between ionic radii of rare earth and transition metal atoms inside the matrix, the rare earth element cannot contribute to promote ferromagnetic behavior in Mn doped ZnO, irrespective of their high individual magnetic moments.

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1. Introduction

Diluted magnetic semiconductors (DMS), in which a small fraction of the native atoms in the hosting non-magnetic semiconductor material is intentionally replaced by magnetic atoms (transition metals or rare earth elements), facilitate an exchange interaction between the hosting electronic sub system and electrons originating in the partially filled 'd' or 'f' levels of the introduced magnetic atoms [1–6]. This in turn enables a control of both the optical and magnetic properties of the end material using external fields in regimes, which can hardly be achieved with other class of materials. Theoretical prediction [7] suggests that the common semiconductors doped with qualified transition metals (TMs) in the range of several atomic percent lead to the development of the room temperature (RT) ferromagnetism in the system making them attractive DMS candidates for potential device applications. However, low Curie temperature in TM doped III-V systems and wide range of controversial reports on anticipated room temperature ferromagnetism (RTFM) in TM doped II-VI systems [8–17] have been the vital constraints for the practical applications of these materials. As a result, various research groups started looking for appropriate magnetic substitutes to fabricate better DMS candidates. In this regard, Mn doped ZnO has already been a popular wide band-gap semiconductor, whose ferromagnetic property has already been extensively explored and established by several scientists including the authors [18]. It has been reported [17,18] that Mn doped ZnO samples with 2 at% Mn concentration show ferromagnetism at room temperature with a low value of saturation magnetization, which is gradually suppressed for higher dopant concentration in the system due to the appearance of some secondary phases [18] in the specimen.

Recently, it has been established that co-doping with shallow donors and acceptors introduces two kinds of defects simultaneously, which could be an improved process for carrier mediated ferromagnetism with large saturation magnetization at high temperature [19,20]. In fact, authors have shown that simultaneous doping of two TMs can fairly increase the saturation magnetization in ZnO system [21]. However, as compared to TM dopants, rare earth (RE) metals are expected to contribute fairly towards the net magnetization, since the 4f electrons in them are localized and the exchange interactions are indirect via 5d or 6s conduction electrons, resulting in high total magnetic moments per atom owing to its high orbital momentum [22]. In fact, the report of giant value of magnetic moment ($4000\mu_B$/atom) in Gd doped GaN [23], fueled the interest of researchers to look for RE based DMS system with interesting results and explanations [24,25]. However, experimental studies for the ferromagnetism of ZnO: RE systems have produced a lot of controversial conclusions [26–29].

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In view of all above observations, attempt has been made by us, to investigate the effect of the presence of a RE dopant along with a TM dopant in ZnO system. In this communication, we report on the influence of simultaneous presence of Mn and Gd/Sm dopants on the structural and magnetic property of ZnO bulk system. Though Gd/Sm has an individual large magnetic moment contribution, simultaneous doping with Mn in ZnO matrix exhibit paramagnetic behavior due to the formation of oxides of rare earths. XRD, SEM and hysteresis studies are performed on the samples to study and explain the changes in structural and magnetic properties of Mn doped ZnO when co-doped with Gd/Sm atoms.

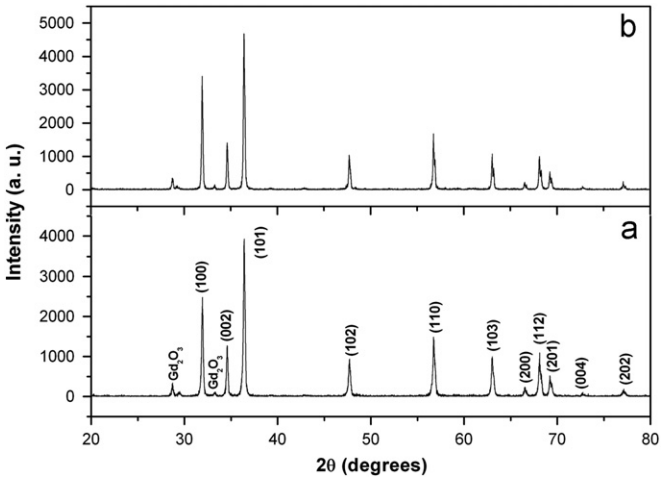

Fig. 1. XRD patterns of $Zn_{0.96}Mn_{0.02}Gd_{0.02}O$ bulk samples sintered at (a) 500 °C and (b) 800 °C.

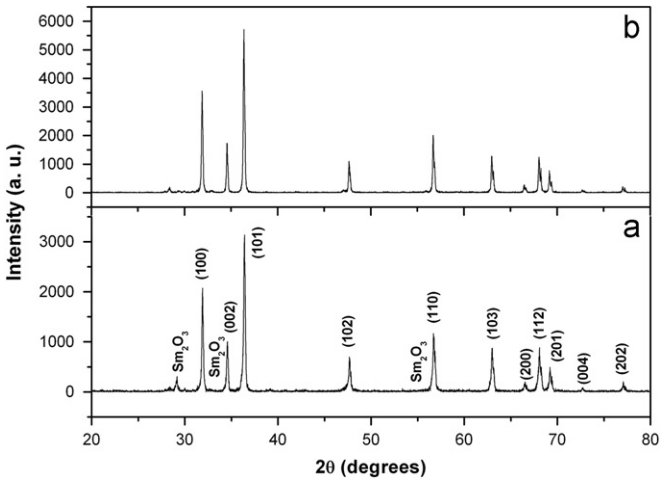

Fig. 2. XRD patterns of $Zn_{0.96}Mn_{0.02}Sm_{0.02}O$ bulk samples sintered at (a) 500 °C and (b) 800 °C.

2. Experimental

Conventional solid state reaction technique was adopted to prepare the bulk samples of $Zn_{0.96}Mn_{0.02}Gd_{0.02}O$ and $Zn_{0.96}Mn_{0.02}Sm_{0.02}O$. For a particular composition, appropriate amount of high pure (99.999%-Sigma-Aldrich) oxides of Zn, Mn, Gd and Sm were taken in an agate mortar and was ground properly for 2 h. The powder was initially heated at 400 °C for 6 h followed by room temperature quenching and grinding. This procedure was repeated five times in order to achieve homogeneous mixture of green powder with smaller particle size. Green powder was palletized after mixing with freshly prepared poly vinyl alcohol (PVA) as binder. Cylindrical pellets with approximately 2 mm thickness and 10 mm diameter were prepared by hydraulic press having 30 t base capacity with a pressure of 10 t/cm^2. Pressed pellets were slowly heated up to 200 °C at a rate of 50 °C/h and kept for 8 h for slow release of PVA binder from the pellets using high-temperature programmable (Eurotherm controller, Model: 2404) vacuum furnace. A slow step sintering schedule was adopted up to 500 °C and 800 °C to obtain highly dense bulk products. X-ray diffraction (XRD) and scanning electron microscopy studies were carried out by Philips diffractometer (Model 1715) and SEM (Philips FEG Xl'30) respectively for structural and morphological analyses. All the hysteresis measurements of the samples were taken at low temperature (10 K) and room temperatures (300 K) using superconducting quantum interference device (SQUID) magnetometer with maximum field of 6 T. Temperature dependent magnetization was recorded at a field of 1000 Oe.

3. Results and discussion

The XRD patterns of $Zn_{0.96}Mn_{0.02}Gd_{0.02}O$ and $Zn_{0.96}Mn_{0.02}Sm_{0.02}O$ bulk samples sintered at 500 °C and 800 °C are presented in Figs. 1 and 2 respectively. As seen from the figure, the overall wurtzite structure of ZnO has not been changed upon doping by Mn and Gd/Sm simultaneously. Distinct impurity peaks of Gd_2O_3/Sm_2O_3 phases are clearly identified in the co-doped samples sintered at 500 °C as well as 800 °C. The percentage of the secondary phases increases with the increase of sintering temperature. Due to the low solubility nature of Mn in ZnO, a small percentage of secondary phases of Mn_3O_4 may exist in the specimen which could not be detected within the XRD instrument limitation. The presence of such secondary phases was well confirmed in our earlier report on Mn doped ZnO [18]. This small percentage of Mn_3O_4 is responsible for showing low temperature hysteresis loop and small cusp in the temperature dependent magnetization curve at 41 K, which is discussed later in detail. Not much variation in the lattice parameters and the c/a value in the RE co-doped samples is recorded in comparison to Mn doped ZnO sample, which is presented in Table 1. It is important to note that the volume of the unit cell has been compressed considerably, upon RE co-doping in comparison to $Zn_{0.98}Mn_{0.02}O$, which is

Table 1
Lattice parameter and unit cell volume of ZnO in $Zn_{0.98}Mn_{0.02}O$; $Zn_{0.96}Mn_{0.02}Gd_{0.02}O$; and $Zn_{0.96}Mn_{0.02}Sm_{0.02}O$ bulk samples sintered at 500 °C and 800 °C.

Sample details	$Zn_{0.98}Mn_{0.02}O$ sintered at 500 °C Ref. [14]	$Zn_{0.98}Mn_{0.02}O$ sintered at 800 °C Ref. no. [14]	$Zn_{0.96}Mn_{0.02}$ $Sm_{0.02}O$ sintered at 500 °C	$Zn_{0.96}Mn_{0.02}$ $Sm_{0.02}O$ sintered at 800 °C	$Zn_{0.96}Mn_{0.02}$ $Gd_{0.02}O$ sintered at 500 °C	$Zn_{0.96}Mn_{0.02}$ $Gd_{0.02}O$ sintered at 800 °C
Parameters						
$a=b$ in Å	3.249	3.249	3.242	3.245	3.243	3.241
c in Å	5.206	5.206	5.193	5.197	5.190	5.190
c/a	1.602	1.602	1.602	1.601	1.600	1.601
V in Å^3	47.59	47.59	47.27	47.39	47.27	47.21

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