

Structural and Magnetic Behavior of Mn Doped ZnO Synthesized By Soft Chemical Route

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ABSTRACT: Nanocrystalline undoped and 5% Mn doped ZnO powders are synthesized by sol-gel route using constituent nitrate and citrate precursors. The physico-chemical characterizations of powders calcined at various temperatures (400-1100 °C), are performed using techniques (XRD and SQUID) to study structural, nano/microstructural, and magnetic properties. XRD patterns clearly revealed the evolution of major wurtzite (ZnO) and minor non-stoichiometric defect cubic spinel phase of $\text{ZnMnO}_{3-\delta}$. Unexpectedly, the magnetic hysteresis loop with its large magnetic parameters are observed at room temperature as soon as the concentration of the minor phase is large enough. The analysis of the unusual room temperature ferromagnetic behavior is presented in this communication based on the dominant contributions of the secondary nanocrystalline non-stoichiometric defect cubic spinel phase of $\text{ZnMnO}_{3-\delta}$.

KEYWORDS: Diluted magnetic semiconductor, soft chemical route, Mn doped ZnO, Room temperature ferromagnetism

I. INTRODUCTION

In the recent past, a surge of interest is observed in the studies of diluted magnetic semiconductor (DMS) oxides due to simultaneous utilization of charge and spin of electrons in a single material to develop new functionalities [1-4]. These DMSs are potential candidates for technological application such as spintronic devices. Recently, this class of materials is studied extensively for better understanding of basic mechanisms of different types of magnetic interactions in diluted system. Among these materials, we focused our attention on undoped and doped ZnO based DMS. Dietl et al reported room temperature ferromagnetic (RTFM) behavior arising from carrier mediated exchange interaction has been predicted for several transition metal (Mn, Fe, Co, etc) doped ZnO and GaN DMSs. [2]. The large amount of experimental work on Mn doped ZnO based DMSs has been reported in literature with contradictory experimental results in favor of RTFM [5-7] when processed at lower temperature and against of RTFM [8,9] when processed at higher temperature. Similar results are obtained in different product (bulk and nanoparticles) forms prepared by different synthesis along with different processing parameters [5-9]. In spite of the tremendous amount of experimental work, the origin of RTFM behavior and the associated energy exchange interactions are not fully understood. In the present investigation, the RTFM behavior of sol-gel synthesized nanoparticles of 5% Mn doped ZnO is discussed in terms of secondary nanocrystalline defect cubic spinel (DCS) phase of $\text{ZnMnO}_{3-\delta}$.

II. EXPERIMENTAL

The sol-gel technique is used to synthesize nanocrystalline undoped ZnO and 5% Mn doped ZnO. Appropriate stoichiometric amounts Zn-nitrate (95%) and Mn-nitrate (5%) were dissolved into distilled water. The mixture of nitrates dissolved into distilled water and the obtained solution is dissolved into citric acid. This mixture mixed well using with magnetic stirrer and transparent gel was obtained. This gel was dried on water bath (96 °C) and calcined for 3hrs at different temperatures (400-1100 °C) in the interval of 100 °C) in air. The same protocol was used for the synthesis of undoped ZnO nanoparticles without adding Mn precursor. The sample of undoped ZnO calcined at 400 °C is labeled as Z(400) and samples of 5% Mn doped ZnO calcined at different temperatures (400-1100 °C) are labeled as ZM(400), ZM(500), ZM(600), ZM(700), ZM(800), ZM(1000), and ZM(1100) respectively. The calcined powders

(400-1100 °C) were characterized by X-ray diffraction (XRD) using BRUKER AXS D8 ADVANCE spectrometer with Cu-K α radiation ($\lambda = 1.541 \text{ \AA}$). The average crystallite size of the powder was estimated using Scherrer's formula. Magnetic measurements at room temperature were performed by using a standard Quantum Design superconducting quantum interference device (SQUID) MPMS magnetometer with maximum field of 10 kOe.

III. RESULTS AND DISCUSSION

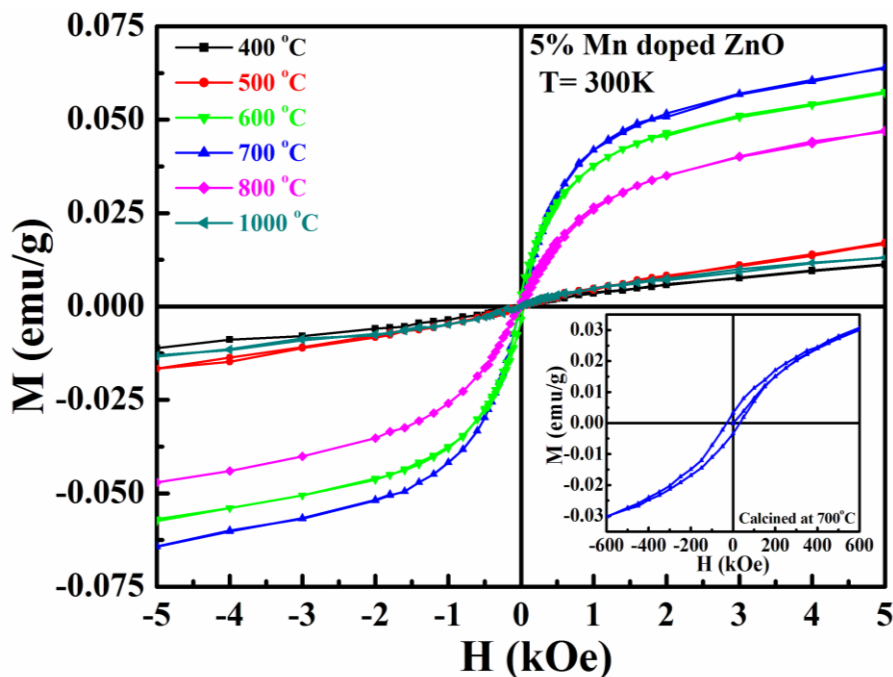


Figure.1. Field dependent magnetization at 300K for 5% Mn doped ZnO calcined at various temperatures

Figure.1 shows field dependent magnetization at room temperature for the 5% Mn doped ZnO calcined at various temperatures (400-1100 °C) in the applied field range of -5 to 5kOe. The undoped and Mn doped samples calcined at 400 °C exhibited magnetic hysteresis loop. Interestingly, the hysteresis loop parameters (M_s , H_c) are found to be enhanced dramatically as soon as the concentration of the minor phase in XRD patterns is large enough up to the calcination temperature 700 °C. In contrast, the magnetic hysteresis loop vanishes slowly for the sample calcined at 1000 °C.

On addressing the origin of strong exchange interaction leading to RTFM behavior in the Mn doped ZnO nanoparticles, various models are proposed in the literature [2-4]. A large number of reports are available in the literature, both theoretical and experimental; on transition metal ions doped ZnO with contradictory to each other [1-9]. Based on the vast experimental data, intrinsic or extrinsic origin of ferromagnetic behavior is studied in Mn doped ZnO with various morphologies, such as bulk [5], films [5,6] and nanoparticles [7] synthesized by the various synthesis methods. Based on the theoretical prediction of RTFM by Dietl et al [2], experimentally Sharma et al [5] found that RTFM in bulk ceramic and laser-ablated transparent thin films of Mn doped ZnO and was attributed to carrier-mediated exchange when Mn concentration is less than 2 at%, the average magnetic moment of Mn was associated with the coexistence of Mn³⁺ and Mn⁴⁺ via a double-exchange mechanism. [10]. Wang et al investigated the effect of Mn dopant concentrations on the magnetic properties of nanoparticles of Zn_{1-x}Mn_xO and reported high temperature RTFM with $x \leq 0.02$; originated due to lattice defects and its absence at $x = 0.05\%$ [11]. Further, it was reported that the interstitial hydrogen could mediate a strong short-ranged ferromagnetic spin-spin interaction between neighboring (Mn atoms) magnetic impurities through the formation of a bridge bond by interstitial hydrogen in Mn-doped ZnO system [12]. It is suggested that the spin parallel state of the (Mn-H-Mn) geometry is more stable than the antiparallel state, which indicates that the H effect is one of the very important factors in Mn doped ZnO DMS [13]. In addition,

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various research groups have proposed interesting mechanisms/models, such as bound magnetic polaron (BMP), magnetic foam to explain RTFM parameters in transition metal ions doped ZnO. In the first case, charge carriers tend to be localized favoring the formation of BMP sometimes referred increases with increment of Mn concentration; while for Mn doping content $x=5$ at%, the ferromagnetism is suppressed and a large paramagnetic effect is observed due to presence of Mn cluster. Kundaliya et al. also discovered above-room-temperature ferromagnetism in low-temperature-processed 2 at% Mn-ZnO pulse laser deposited thin film system. However, they demonstrated that ferromagnetism originated from oxygen-vacancy-stabilized metastable phase, rather than by carrier-mediated exchange [6]. Garcia et al. showed that in PLD deposited thin films of Zn-Mn-O system; the RTFM as charge transfer ferromagnetism in the literature [14]. In the second case, Straumal et al. have proposed the concept of specific grain boundary area and its influence/role in terms of magnetic foam model to explain RTFM in nanograined Mn doped ZnO [15]. More complexity is very recently introduced by the observation of RTFM behavior in carbon doped ZnO [16, 17]. Pan et al reported RTFM in carbon doped ZnO Films deposited by pulsed laser deposition with Curie temperature higher than 400K and this ferromagnetism is due to Zn-C system in the ZnO environment [16].

Another unique and interesting experimental aspect has also been introduced in this field of RTFM in magnetic semiconductors by the observation of similar behavior in undoped and capped nanocrystalline non-magnetic oxides like ZnO [18, 19]. In pure (undoped) oxides systems, Sunderasan and Rao have found RTFM hysteresis loops and assigned the origin to the oxygen and cation vacancies which are commonly encountered [19]. These assignments are understood in terms of intrinsic cationic/anionic defects, extrinsic defects associated with the various species chemisorbed on the surface of the nanoparticles that could give rise to the magnetic moments.

In view of these, complex models are proposed, it is more difficult to understand the RTFM behavior in doped ZnO system and its real origin of magnetic interactions. It is well known that bulk ZnO is diamagnetic with susceptibility -1.63×10^{-7} emu/g.Oe at room temperature [20]. In the present case, RTFM behavior in nanocrystalline undoped and Mn doped ZnO without secondary phase is understood in terms of intrinsic cationic/anionic defects, extrinsic defects associated with the various species chemisorbed on the surface of the nanoparticles of undoped and Mn doped ZnO [18,19]. The unique observation matches well with the appearance of the secondary phase, albeit a small amount of DCS-ZnMnO_{3.8} phase in the temperature range 600-800 °C; suggesting a possible role of the secondary phase in exhibiting complex magnetic behavior. Sometimes, the secondary phase is not detected with lower dopant concentration but detected with higher concentration using XRD, HRTEM techniques etc. But it is observed that the secondary phase causes dramatic changes in the magnetic behavior of Mn doped ZnO. In the present case, the dopant concentration is purposely increased to 5% for the special purpose of the evolution of secondary phase in Mn doped ZnO and studied the changes in the magnetic behavior.

According to the XRD results, well concentrated nanocrystalline secondary cubic spinel phase of DCS-ZnMnO_{3.8} in addition to the major wurtzite phase is evolved in the nanoparticles of 5% Mn doped ZnO at 700 °C where the saturation magnetization and coercivity were observed to be enhanced very well. The crystallite sizes of each of the calcined powders measured using Scherrer's formula and the corresponding obtained magnetic parameters (Magnetization M_s and coercivity H_c) are given in the Table.1. Experimentally, it is clearly observed that the magnetic parameters were enhancing in the calcinations temperature range i.e.600-700 °C where secondary nanocrystalline ZnMnO_{3.8} phase was observed. Interestingly, the magnetic parameters decreases (from 800 °C) with the further

Table.1. Structural evolution, crystallite size according to XRD patterns and Magnetic data of undoped ZnO (at 400 °C) and 5% Mn doped ZnO at various temperatures.

Sample	Structural evolution according to XRD patterns	Crystallite size (nm)	Magnetization M_s (emu/g)	Coercivity H_c (Oe)
Z(400)	Wurtzite	41	0.006-0.008	7~8
ZM(400)	Wurtzite	24	0.085	12
ZM(500)	Wurtzite	27	0.14	15
ZM(600)	major wurtzite+ minor DCS-ZnMnO _{3.8}	28	0.176	20
ZM(700)	major wurtzite+ minor DCS-ZnMnO _{3.8}	46	0.195	34
ZM(800)	major wurtzite+ minor DCS-ZnMnO _{3.8}	77	0.170	28
ZM(1000)	Wurtzite	87	0.095	0

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increase in the calcinations temperature and became zero as the concentration of the secondary phase decreases. During low temperature processing (600-800 °C), it may be possible that some intrinsic cationic/anionic defects and the extrinsic defects associated with the organic molecules; contributing few radicals (OH^\cdot , CH^\cdot , COO^\cdot) /species which are subsequently chemisorbed during cooling process on the surface of nanocrystalline DCS-ZnMnO_{3-δ}. Further, the long range strong ferromagnetic interaction via these intrinsic and extrinsic defects and their interaction with Mn ions in the nanocrystalline DCS-ZnMnO_{3-δ} caused strong RTFM ordering in 5% Mn doped ZnO system. Recent studies have shown that applying high field to Mn doped ZnO system would be a crucial factor in order to obtain RTFM behavior and the connection between nanocrystalline secondary phase and magnetism has been thought as an important factor for the RTFM. In our earlier publication, separately synthesized non-stoichiometric DCS-ZnMnO_{3-δ} exhibited RTFM with $M_s = 0.0035 \text{ emu g}^{-1}$ and $H_c = 22 \text{ Oe}$ but with the application of high field as 5 kOe [21].

IV. CONCLUSION

Nanocrystalline 5% Mn doped ZnO exhibited interesting magnetic behavior which is explained on the basis of magnetic interactions between intrinsic cationic/anionic and extrinsic (chemisorbed species) defects with local adsorbed paramagnetic species in the nanocrystalline secondary phase DCS-ZnMnO_{3-δ}.

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