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Localized ferromagnetic charge ordering through charge density analysis in nano sized diluted magnetic semiconductor Co^{2+}:ZnO

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ABSTRACT

Nano sized diluted magnetic semiconductor Co^{2+}:ZnO (with composition $Zn_{0.99}Co_{0.01}O$) was prepared by sol–gel method and studied for the effect of annealing on ferromagnetic charge ordering using charge density studies. Powder XRD data sets of the samples annealed at various temperatures (500, 600, 700, 800 and 900 °C) have been investigated by the Rietveld refinement analysis and the charge density distribution using the maximum entropy method (MEM). The mid bond electron densities between the Zn(Co) and O atoms are analyzed to understand the origin of ferromagnetic behaviour between the temperature range 600–700 °C. $Zn_{0.99}Co_{0.01}O$ is found to switch "on" the ferromagnetic behaviour range 600–700 °C and then to switch "off". The charge ordering that results in ferromagnetic occurrence is dealt for the first time through charge density route.

1. Introduction

Research interest on the spintronics materials is developing fast in recent years [1] due to their potential applications. Spintronics devices can manipulate the spin of electrons and spintronics units are capable of consuming very low power at high speed. For practical applications, ferromagnetic diluted magnetic semiconductor (DMS) with Curie temperatures (T_C) well above room temperature are desired.

Among several candidates of oxide based DMS materials with a high T_C, the $Zn_{1-x}Co_xO$ DMSs are of current interest as they are theoretically expected to have high T_C values, a consequence of the large gap and effective mass. Room temperature ferromagnetism in transition metal doped ZnO was originally predicted by Dietl et al. [2] and Sato [3]. These studies are the basis for many research works done on ZnO based DMS.

Ueda et al. [4] have reported on the room temperature ferromagnetism in Co doped ZnO prepared by pulsed laser deposition (PLD) on the sapphire substrate. Thin films [5,6] and bulk forms [7,8] of Co doped ZnO prepared under various growth conditions have been reported with a wide variety of results. Deka et al. [9] reported ferromagnetism in hydrogenated $Zn_{0.95}Co_{0.05}O$ samples and Manivannan et al. [10] predicted the same due to oxygen vacancies created by hydrogenation. Many other works [11–16] reported that the oxygen vacancies and the interstitial Zn defects play a crucial role in the ferromagnetic behaviour in Co doped ZnO. Rubi et al. [17] found that the ferromagnetism in ZnO doped with Co can be switched on and off by low temperature annealing in nitrogen and oxygen environments suggesting that n-type defects are important to induce ferromagnetic coupling between $Zn^{2+}(Co^{2+})$ ions. The DMS material $Zn_{0.99}Co_{0.01}O$ grown without deliberate incorporation of such defects has been studied extensively and exhibits only paramagnetism with weak local antiferromagnetic super exchange, [18,19] but weak ferromagnetism can be induced by vacuum annealing, [20] and stronger ferromagnetism can be achieved by growth under lower O_2 partial pressures [21,22] both linked to introduction of shallow donor defects. Quantitatively reversible 300 K ferromagnetic ordering in $Zn_{0.99}Co_{0.01}O$ was demonstrated by Zn vapor diffusion ("on" state of ferromagnetism) and subsequent aerobic re-oxidation ("off" state), attributed to introduction and removal of the shallow donor, interstitial zinc (Zn) [23].

These reports highlight the importance of growth conditions such as synthesis temperature and gaseous environment used during the preparation on the appearance of ferromagnetism in the material.

The ferromagnetic behaviour in $Zn_{0.99}Co_{0.01}$ depends more on the thermal annealing process and hence in this work the authors report the effects of thermal annealing in Ar/H_2 environment on the charge ordering in $Zn_{0.99}Co_{0.01}O$ grown by sol–gel method from charge density analysis using accurate X-ray diffraction measurements.

2. Experimental

The system $Zn_{0.99}Co_{0.01}O$ was prepared as solutions and polycrystalline nano powders using sol–gel technique with zinc acetate

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(Fluka), cobalt acetate (Merck), as precursor materials and methanol as solvent. After weighing the appropriate amounts of the constituents, they were all mixed with a magnetic stirrer for 8 h at room temperature until a transparent solution was obtained. The prepared nano powders were made to adhere on a glass substrate in order to be ready for XRD measurements. To improve adhesion of the resultant material on the glass substrate, triethanolamine was used in the solution. Samples were preheated at varying temperatures and time. This process was repeated eight times in order to achieve dense and homogeneous samples. The final product in the powdered form was annealed individually in Ar/H_2 atmosphere at temperatures in steps of 100 °C from 500 to 900 °C. X-ray powder data sets were collected for all the annealed samples using monochromatic incident beam of CuKα (1.54056 Å) radiation using Rigaku X-ray diffractometer, with 2θ ranging from 10° to 90°.

3. Rietveld refinement

The well known Rietveld [24] method is a method for refining crystal structure from powder diffraction profile. In this work, the Rietveld [24] analysis was performed for all data sets using the software package JANA 2006 [25].

In refining the X-ray powder data, the space group was set as $P6_3mc$ and the initial cell parameters were introduced as a=3.24 and c=5.20 Å with unique positions of the Zn and O atoms in the unit cell taken as (0.333, 0.666, 0.5) and (0.333, 0.666, z) where z is refinable (which was initially taken as 0.875). The refined and fitted Rietveld profiles for $Zn_{0.99}Co_{0.01}O$ are presented in Figs. 1–5. The refined structural parameters and the reliability indices are given in Table 1. The results show that the lattice parameters and the cell volume increases up to 600 °C then decreases at 700 °C followed by an increasing trend thereafter. The FWHM derived from the profiles are used for the size determination of the nano crystals using the software GRAIN [26] and found to be in the range 27–48 nm for the temperature range 500–900 °C. The values presented in Table 1 show the expected increasing trend in the particle size due to increasing annealing temperature. The thermal parameters and the structure factors evolved from the refined profiles were further utilized for the estimation of charge density in the unit cell of $Zn_{0.99}Co_{0.01}O$.

4. Charge density from maximum entropy method (MEM)

The origin of charge ordering can be understood from the accurate electronic structure inside the unit cell and this can be achieved by constructing the charge density from structure factors using the best possible mathematical model like maximum entropy method (MEM). This method was successfully introduced to X-ray crystallography for constructing charge density in the unit cell by Collins [27] in 1982. MEM infers electron densities in such a way that they provide the maximum

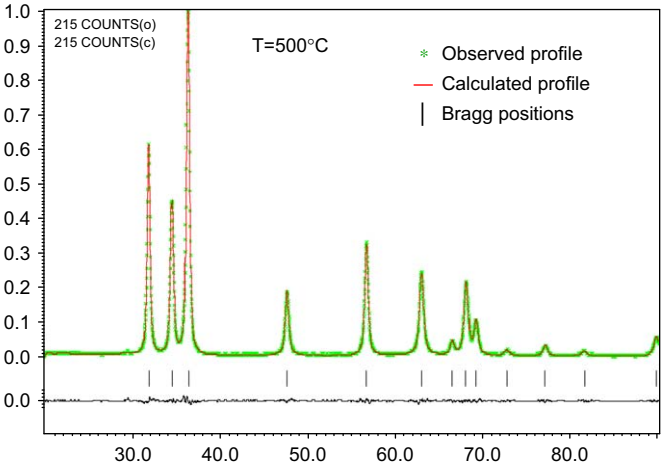

Fig. 1. Rietveld refined profile for $Zn_{0.99}Co_{0.01}O$ at 500 °C.

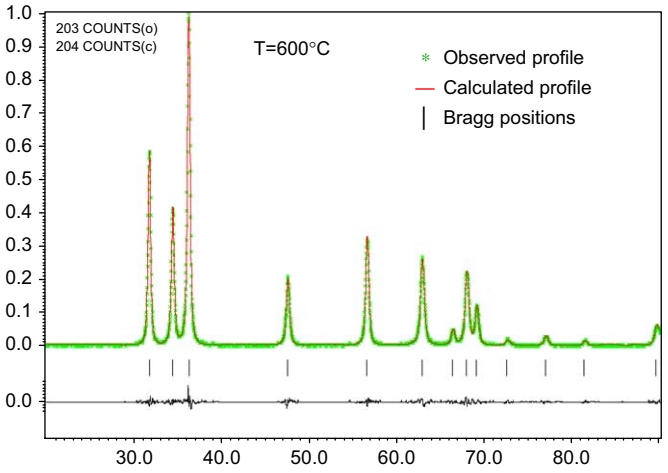

Fig. 2. Rietveld refined profile for $Zn_{0.99}Co_{0.01}O$ at 600 °C.

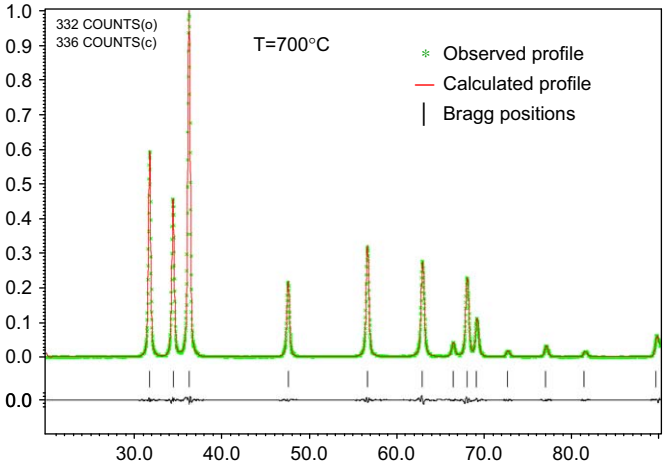

Fig. 3. Rietveld refined profile for $Zn_{0.99}Co_{0.01}O$ at 700 °C.

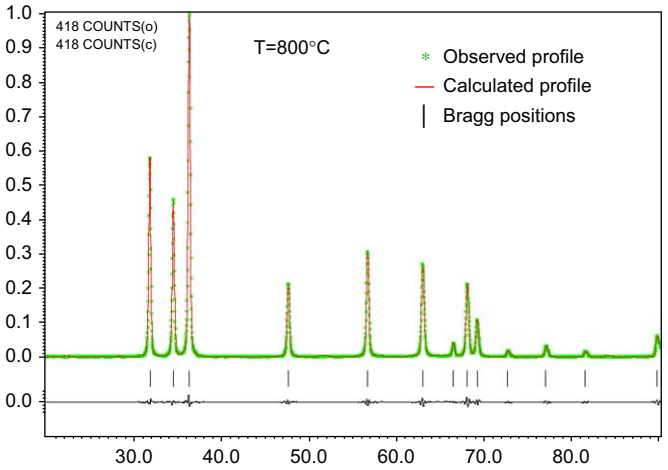

Fig. 4. Rietveld refined profile for $Zn_{0.99}Co_{0.01}O$ at 800 °C.