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Room temperature ferromagnetism in undoped and Mn doped CdO nanostructures

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ABSTRACT

$Cd_{1-x}Mn_xO$ (x=00–0.07) nanostructures were synthesized and their structural, optical and magnetic properties were investigated. The shift of diffraction peaks towards lower angle side with increase of Mn content indicates the incorporation of Mn^{2+} ions into the CdO lattice. The values of optical band gaps were calculated at each value of Mn concentration. The values of band gap were increased by increasing the Mn concentrations as a direct consequence of the quantum confinement effect. The undoped CdO [$Cd_{1-x}Mn_xO$ (x=0.00)] nanostructure shows weak ferromagnetic nature at room temperature. The ferromagnetic nature increases consistently with increase of Mn concentrations from x=0.01 to 0.05 and then slightly drops for x=0.07. As there were no magnetic impurities present in the samples, we assume that the origin of ferromagnetism in the undoped CdO nanostructures could be due to formation of CdO structure in triplet state (S=1). However, the consistent increase of magnetic nature with Mn doped (x=0.01–0.05) CdO nanostructures might be attributed to the ferromagnetic coupling between the spins and enhancement of spin concentrations due to entering of Mn atom into the lattice. The sudden drop of ferromagnetic nature at x=0.07 may be due to the presence of anti-ferromagnetic coupling.

1. Introduction

Recently, the interest in studying nanostructured metal oxide semiconductors has increased among researchers because of quantum size effect associated with the low dimensionality, which causes unique size and shape dependent physical and chemical properties. Due to the size and shape tunable properties of the nanostructured materials, it has widely been used in many areas of science such as; chemistry, physics and materials science from a technological point of view. They are being used in a variety of applications such as flat panel displays, light emitting diodes, biological labels and photovoltaic solar cells [1].

CdO is one of the most important semiconductors which have attracted great attention to the world wide scientists due to its interesting properties such as; higher conductivity and transmission with prominent applications. It is an n-type wide band gap semiconductor with a direct band gap at ~2.5 eV, and a narrower indirect band gap ~2.0 eV [2]. CdO nanostructure is also of particular interest because of their potential use as optoelectronics materials [3]. In general, semiconductors doped with transition metal, popularly known as dilute magnetic semiconductor (DMS) where a fraction of the host cations can be substitutionally replaced by magnetic ions, can be exploited for basic research and various technological applications [4]. It is well studied that the doping of transition metals such as Mn [5], Cu [6] and Co [7] in semiconducting nanostructures opens the possibilities of building up new class of materials with novel properties. DMS are more attractive for their promised functionalities in the emerging field of spintronics [8]. These spintronic devices can be used in non-volatile memory, magnetic sensors, spin valves and spin light emitting diodes. Synthesis of II–VI based DMS provides a material with both semiconducting and magnetic properties [7]. In view of above discussed studies and applications of CdO nanostructures motivated us to perform a systematic study on undoped and Mn doped CdO nanostructures. In spite of various potential applications and technological importance, systematic investigations on this system are very limited. Thus in the present study, we have successfully synthesized $Cd_{1-x}Mn_xO$ (x=0.00, 0.01. 0.03, 0.05 and 0.07) nanostructures through chemical co-precipitation method. The synthesized nanostructures were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), energy dispersive X-ray analysis (EDX), Ultraviolet–visible (UV–visible) and vibrating sample magnetometer (VSM) measurements. The effect of different doping concentrations of Mn in CdO

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nanostructures on structural, optical and magnetic properties has been investigated and compared with those observed for undoped CdO nanostructures.

2. Experimental

2.1. Synthesis

$Cd_{1-x}Mn_xO$ ($x=0.00$) nanostructures have been synthesized at room temperature by simple and low cost chemical method using $Cd(CH_3COO)_2 \cdot 2H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$ and ammonia solution 25% (0.91) pure as starting chemicals. All chemicals were used without further purification. For the synthesis of undoped CdO nanostructures, a aqueous solution of appropriate amount of $Cd(CH_3COO)_2 \cdot 2H_2O$ was prepared in distilled water. The prepared solution was stirred for half an hour and subsequently ammonia solution was added to the solution drop wise until desired pH was reached. While adding the ammonia, a white precipitate was formed. The stirring of solution was continued for another few hours. The white precipitate was kept to settle down for 5 h. Thereafter, the solution was filtered and washed repeatedly with distilled water to remove un-reacted materials. The obtained precipitate was dried at 80 °C and then grinded to fine powder with the help of mortar and pestle. The resulting powder was calcined at 400 °C for 2 h to obtain the final product. Further, the $Cd_{1-x}Mn_xO$ ($x=0.01$. 0.03, 0.05 and 0.07) nanostructures were synthesized by mixing the suitable amount of $Mn(CH_3COO)_2 \cdot 4H_2O$ and $Cd(CH_3COO)_2 \cdot 2H_2O$ solution in the initial stage of preparation. The rest of the process was kept same we have followed for the synthesis of undoped CdO nanostructures.

2.2. Characterization tools

The structural, optical and magnetic properties of synthesized products were investigated using XRD, TEM, EDX, UV–visible and VSM measurements. The XRD of powder samples was performed by using a Philips X'Pert Pro diffractometer in 2θ range of 30°–80° with CuKα radiation ($\lambda=1.54$ Å) at room temperature to obtain crystal phase and structural information of the samples. The size and shape of the samples were determined using TEM measurements using a Transmission electron microscope (Hitachi Model H-800 instrument) consisting of a tungsten filament. The EDX measurements of the synthesized nanostructures were performed to identify the presence of key elements in the samples along with the quantitative analysis to know the stoichiometery. The optical absorption spectra of the nanostructures were recorded using Hitachi 330 Ultraviolet visible spectrometer in the solution form in ethanol environment to study the variation in optical band gap with dopant concentrations. In order to study the magnetic evolution in synthesized samples, vibrating sample magnetometer (VSM) measurements have also been done at room temperature.

3. Results and discussion

3.1. Structural studies

The XRD patterns of synthesized samples were presented in Fig. 1. The XRD patterns have been indexed on the basis of data available with the JCPDS card no. 73-2245. The five most prominent peaks were indexed as (111), (200), (220), (311) and (222) planes corresponding to cubic structure of CdO. These peaks were nicely matched with the JCPDS card no. 73-2245 of cubic CdO. In

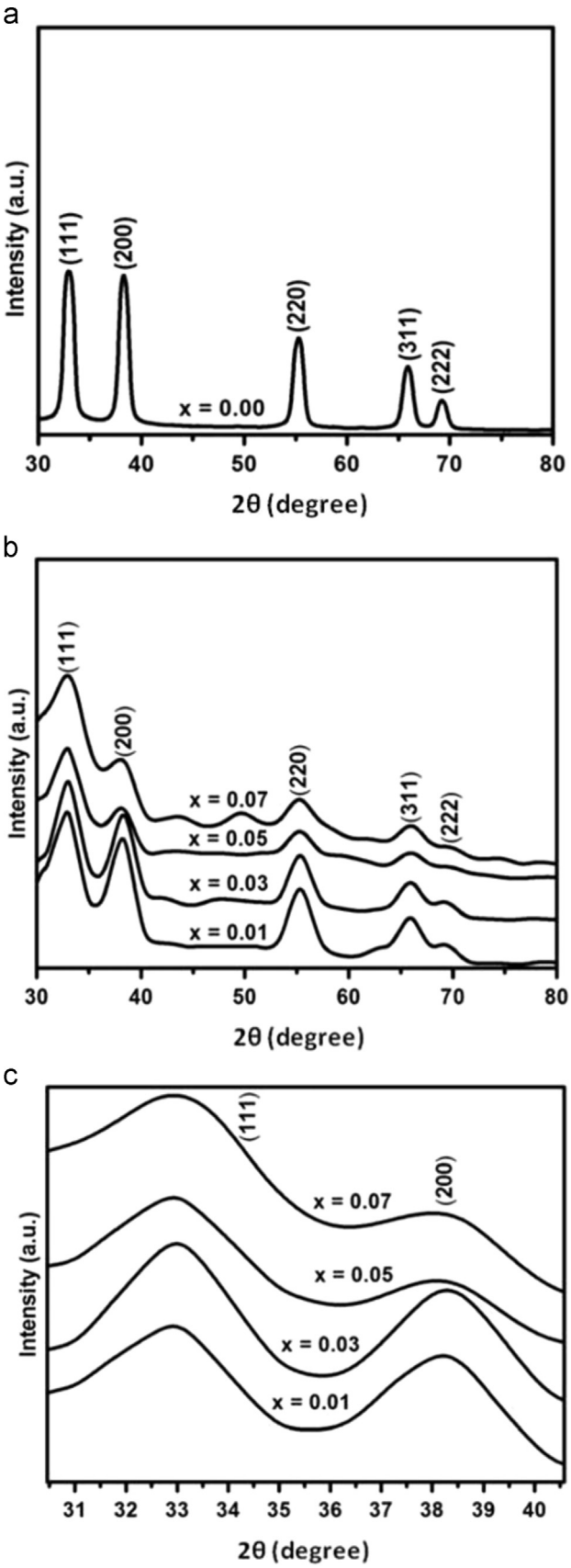

Fig. 1. Room temperature powder X-ray diffraction (XRD) pattern of $Cd_{1-x}Mn_xO$ nanostructures at (a) $x=0.00$ (b) $x=0.01$, 0.03, 0.05 and 0.07 (c) magnified XRD pattern of (111) and (200) planes for $x=0.01$, 0.03, 0.05 and 0.07.