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Optical and magnetic properties of $Sn_{1-x}Mn_xO_2$ dilute magnetic semiconductor nanoparticles

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ABSTRACT

$Sn_{1-x}Mn_xO_2$ (x = 0.05, 0.10 and 0.15) nanoparticles with tetragonal structure have been successfully synthesized by solvothermal method using oxalate precursor route. The oxalate precursors and its corresponding oxides were characterized by powder X-ray diffraction (PXRD), thermogravimetric (TG), fourier transform infrared (FTIR) and transmission electron microscopic (TEM) studies. PXRD studies showed the highly crystalline and monophasic nature of the solid solutions. The shifting of X-ray reflections towards higher angle is attributed to the incorporation of Mn^{2+} ions in SnO_2 host lattice. The average particle size was found to be in the range of 5–11 nm. Reflectance measurements showed blue shift in energy band gap which increases with increasing Mn^{2+} concentration. Surface area of these nanoparticles (59–388 m^2/g) was found to be high which increases with increasing the dopant ion concentration. Mn-doped SnO_2 showed distinct magnetic behaviour with different manganese concentration. $Sn_{1-x}Mn_xO_2$ (x = 0.05 and 0.10) revealed the parasitic ferromagnetism, however on increasing x = 0.15, sample showed paramagnetic behaviour.

1. Introduction

Nanomaterials have fascinated the researchers in the recent years because of their unusual optical, magnetic and electrical properties as compared to their bulk counterparts. Oxide based dilute magnetic semiconductors have attracted considerable attention both theoretically and experimentally due to their potential applications in spintronic devices [1–3]. Tin dioxide (SnO_2) is an n-type transparent semiconductor with a direct energy band gap in the range of 3.5–3.8 eV [4–6]. SnO_2 has a rutile (TiO_2) type tetragonal structure with $P4_2/mnm$ space group. Due to its outstanding physical and chemical properties, SnO_2 has many applications in the field of catalysis, transparent conducting electrodes, flat-panel displays, solar cells, optoelectronic devices, gas sensors, transistors and lithium ion batteries etc. [7–11]. Transition metal doped SnO_2 is considered as a promising material for the development of multifunctional magneto-optical devices due to its high optical transparency and room temperature ferromagnetism.

Mn-doped SnO_2 nanoparticles developed by sol–gel [12,13] and ceramic [14] methods are expected to be a promising material for the origin of room temperature ferromagnetism in the series of dilute magnetic semiconductors. However, the ferromagnetism vanished when the solid solution sintered at high temperatures, such as, 800 °C [15]. Recently, it has been reported that 5% and 10% Mn-doped SnO_2 nanoparticles synthesized at 800 °C exhibit ferromagnetism, however, at low temperature (300 °C) samples behaved paramagnetically [16]. The paramagnetic behaviour in Mn-doped SnO_2 was also observed in few reports [17,18]. It has been observed that the magnetic properties strongly depend on the dopant concentration, fabrication method and processing condition. Recently it has been reported that the annealing of Mn-doped SnO_2 influences the magnetic properties of materials [19]. FMR line was identified in $Sn_{1-x}Mn_xO_2$ (x = 0.005) system annealed at 400 °C which attributed to ferromagnetic phase [19].

It is well known that the band gap of semiconductors can be tuned by controlling the size of the particles which increase with decrease in the particle size due to the quantum size effects. The size of the nanoparticles can be controlled by the soft chemical synthesis methods. Recently, the oxalate precursor mediated modified solvothermal method has been used for the preparation of several transition metal doped oxide based semiconductors such as nanocrystalline $Cd_{1-x}M_xO$ [20–22] and $In_{2-x}M_xO_3$ [23–25] (M = Mn, Ni and Co) with controlled morphology. This method is cost effective as the chemical synthesis has been carried out in a simple refluxing glass assembly instead of an expensive autoclave. Also, the oxalate precursor helps in the synthesis of pure and

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homogeneous oxide nanoparticles at low decomposition temperature. In this paper, we present our investigation to understand the optical and magnetic properties of Mn-doped SnO_2 nanoparticles prepared by modified solvothermal method through oxalate precursor route.

2. Experimental

$Sn_{1-x}Mn_xO_2$ (x = 0.05. 0.10 and 0.15) nanoparticles were synthesized by modified solvothermal method using oxalate as the precursor. The aqueous solutions of metal salts (0.1 M) were prepared in double distilled water. Stoichiometric quantities of tin chloride dihydrate (Merck, 97%) and manganese acetate tetrahydrate (CDH, 99%) were well mixed in 500 mL round bottom flask with constant stirring. 75 mL of diammonium oxalate monohydrate (Merck, 99%) was added into the mixture slowly with constant stirring to minimize the agglomeration and to promote faster precipitation. A pale yellow suspension was immediately formed. Approximately 75 mL of ethanol (Merck) was also added to the reaction mixture in order to reduce its boiling temperature and the mixture was refluxed for 12 h at ~70 °C in a closed environment so that the volume of reaction mixture remains constant. The precipitate was separated from the solution by centrifugation and washed with double distilled water to remove water soluble impurities and finally with acetone. The precipitates were dried in oven at 55 °C for 1 h. Pale yellow powders of Mn-doped tin oxalate precursors were obtained. On the basis of thermogravimetric analysis, grey powders of $Sn_{1-x}Mn_xO_2$ (x = 0.05, 0.10 and 0.15) nanoparticles were obtained by the decomposition of precursors at 600 °C for 6 h in nitrogen atmosphere.

Thermogravimetric (TG) analysis of the precursor was carried out on EXSTAR 6000 instrument in nitrogen atmosphere at a heating rate of 5 °C min^{-1} with alumina as a reference sample. On the basis of TG results, the oxalate precursors were calcined at 600 °C for 6 h in nitrogen atmosphere. FT-IR spectra of the oxalate precursor were recorded in the wavenumber range of 500–4000 cm^{-1} on a Bruker FTIR spectrophotometer under neat condition on ZnSe crystals. Powder X-ray diffraction (PXRD) studies were carried out on a Bruker D8 advance diffractometer using Ni-filtered Cu Kα X-rays of wavelength (λ) 1.54056 Å. Normal scans were recorded with a step size of 0.05° and a step time of 1s. Raw data was subjected to background corrections and $K\alpha_2$ lines were stripped off.

The grain size and morphology of nanoparticles have been studied by transmission electron microscopy (TEM) using FEI Technai G^2 20 transmission electron microscope with an accelerating voltage of 200 kV. The TEM specimens were prepared by dispersing the samples in ethanol and placing a drop of the dispersed sample on a copper grid. Room temperature optical properties were measured by UV–Visible spectrophotometer (ocean optics lambda-25 UV–Visible spectrophotometer) in reflection mode. For reflectance spectra pellets were prepared and $BaSO_4$ was used as a reference sample.

Specific surface area of the powder samples were determined by Brunauer–Emmett–Teller (BET) method and the pore parameters of the samples were determined by Barrett–Joyner–Halenda (BJH) method at 20 points with the help of surface area and pore size analyzer (Make: Quantachrome instruments, USA; Model: NOVA 2000e). Samples were degassed at 250 °C for 3 h in vacuum for the removal of adsorbed gases. After degassing, specific surface area was obtained from the nitrogen adsorption experiments measured at 77 K. Magnetic properties were measured using a Quantum design physical properties measurement system at temperature ranging from 5–300 K at an applied magnetic field of 1 kOe. Magnetization versus magnetic field curves were measured at 5 K.

3. Results and discussion

The thermal decomposition of Mn-doped tin oxalate precursor was studied from TG measurements under nitrogen flow at the heating rate of 5 °C/min. Fig. 1 shows the TG plots of $Sn_{1-x}Mn_xC_2O_4$ (x = 0.05, 0.10 and 0.15) precursor. The precursor started losing weight as soon as it is heated. A continuous weight loss of 1–2% is observed till 100 °C, which may be attributed to the removal of less bonded adsorbed water. The major weight loss in the temperature range 200–350 °C occurred, leading to the formation of oxides by the removal of CO.

Fig. 2 shows the FTIR spectra of $Sn_{1-x}Mn_xC_2O_4$ (x = 0.05, 0.10 and 0.15) precursor. The band at around 3420 cm^{-1} is attributed to the –OH stretching of water which arises due to the presence of adsorbed water in the oxalate precursor. Two narrow bands appeared at around 2881 and 2823 cm^{-1} may be assigned to the stretching vibrations of O—C=O bonds. The strongest IR band appeared at 1598 cm^{-1} is due to the C—O bonds. However, the bands show clear splitting which may led to the presence of two

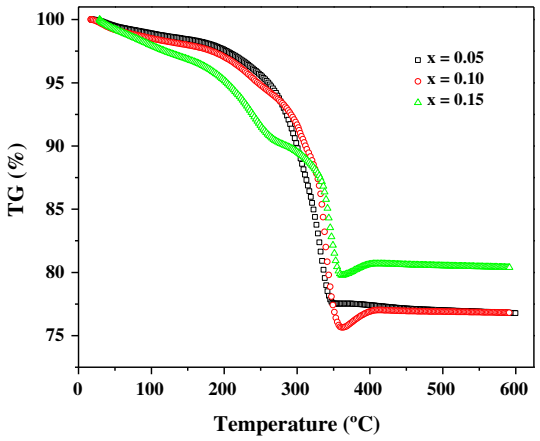

Fig. 1. TG curves of $Sn_{1-x}Mn_xC_2O_4$ nano-precursors for x = 0.05, 0.10 and 0.15.

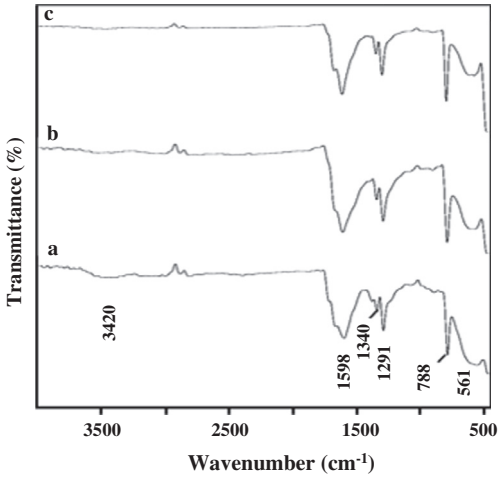

Fig. 2. FTIR spectra of $Sn_{1-x}Mn_xC_2O_4$ nano-precursors for x = (a) 0.05, (b) 0.10 and (c) 0.15.

groups of C—O units with different bond lengths [26]. The bands appeared in the wavenumber region of 474–620 cm^{-1} is due to the vibration of antisymmetric Sn—O—Sn mode of tin oxide and the band at around 788 cm^{-1} is due to the lattice mode [27]. These results are in good agreement with the earlier reports [28,29]. FTIR spectra of Mn-doped tin oxalate showed characteristic bands of SnC_2O_4 with slight shifting of peaks, indicating the incorporation of manganese in Sn^{4+} lattice site.

Powder X-ray diffraction studies of the oxalate precursors obtained by solvothermal method showed the amorphous nature of SnC_2O_4 at room temperature. Fig. 3 shows the powder X-ray diffraction patterns of $Sn_{1-x}Mn_xO_2$ (x = 0.05, 0.10 and 0.15) nanoparticles obtained by heating the precursors at 600 °C for 6 h in nitrogen atmosphere. All the reflections could be indexed on the basis of tetragonal cassiterite structure of monophasic SnO_2 (JCPDS No. 77-0452). However, monotonic shift of all the diffraction peaks towards higher angle is observed, which may be attributed to the incorporation of Mn^{2+} in SnO_2 matrix. The unit cell parameter 'a' has been calculated which comes out to be 4.717 Å, 4.699 Å and 4.687 Å respectively and 'c' was found to be 3.177 Å, 3.176 Å and 3.149 Å respectively, which shows the slight decrease in unit cell dimensions. The contraction of lattice is due to the decrease in the interatomic spacing which results from the substitution of smaller Mn^{2+} ions (0.66 Å) for larger Sn^{4+} ions (0.69 Å) [30]. It has been observed that intensity of peaks increased and become