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Role of Co doping on structural, optical and magnetic properties of TiO_2

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ABSTRACT

The paper deals with the influence of Co doping on the structural, optical and magnetic properties of TiO_2. XRD and Raman measurements confirmed single phase anatase structure of the Co doped TiO_2 without having any impurity phases. The results are explained in terms of the broadening of peaks and small shift of Raman scattering modes, which is caused by the generation of defects such as vacancies and interstitials and owe their presence due to the microscopic structural disorder of oxygen lattice. 10% Co doped TiO_2 exhibits room temperature ferromagnetic behavior with a 0.937 emu/g saturation magnetization and 65 Oe coercivity. Optical spectra have red shift with increasing Co in TiO_2, due to *sp–d* exchange interactions. These interactions may be responsible for the ferromagnetic properties of the samples and the carriers are spin-polarized to mediate the ferromagnetic ordering.

1. Introduction

The emerging field of Spintronics requires either spin ordered (DMS) or multilayered structures (Spin Valves). There is a great deal of discussion about the cause of magnetic ordering in Dilute Magnetic Semiconductors (DMS) systems. On the other hand, a large number of papers tend to emphasize the genuineness of the ordering being due to doping. Room temperature ferromagnetism can be achieved in semiconducting/insulating oxide materials, when doped with few percent of Transition Metal (TM) ions and due to interstitial vacancies created at host lattice position as well as oxygen vacancies [1–8]. Spin injection into non-magnetic semiconductors have been tried by many research groups due to the potential to create new classes of Spintronics devices [9]. The most studied DMS systems are characterized by *sp–d* exchange between the *s*, *p* free carriers, and the *d* states of the transition metal dopant [10]. Due to these interactions, the carriers are spin-polarized and able to mediate ferromagnetic ordering of the magnetic moments of transition metal ions doped into the semiconductor lattice [11]. This results in correlation of ferromagnetism with carrier concentration and provides conditions for using the material as an effective spin injector [12].

Matsumoto et al. [13] have reported that Co-doped TiO_2 thin films exhibited room temperature ferromagnetism. Park et al. [14] have investigated electronic structures of anatase $Ti_{1-x}Co_xO_2$ and suggested that oxygen vacancies near Co sites can drastically influence the magnetic properties of the sample. Hong et al. [15] have also reported the ferromagnetism in transition metal doped TiO_2 thin films. It is also reported [10–15] that room temperature ferromagnetism in V/Cr/Fe/Co/Ni doped thin films must have its origination due to the transition metal doped TiO_2 matrices. Sharma et al. [16] have reported that $Ti_{1-x}Mn_xO_2$ films with $x \geqslant 0.05$ exhibit ferromagnetic ordering at room temperature which arises due to formation of bound magnetic polarons. Pore et al. [17] have reported that TiO_2 thin films doped with cobalt oxide showed magnetic response with certain hysteresis and coercive fields. Mohanty et al. [18] have reported that TiO_2 and Co-doped TiO_2 (CTO) thin films grown by pulsed laser deposition at various oxygen pressures exhibit room temperature ferromagnetism (RTFM) independent of their phase. Patel et al. [19] have reported that nanotubes of TiO_2 (B) phase doped with 5 at.% of Vanadium (V) exhibited ferromagnetic character with clear hysteresis loop at room-temperature and explained the magnetic behavior due to formation of bound magnetic polarons (BMP). Santara et al. [20] have reported that Co doped TiO_2 nanoparticles grown by ball milling method with different Co concentrations showed high temperature ferromagnetism. They have studied defect structure using structural and optical properties and explained the observed RTFM due to defects related to oxygen vacancies. Bapna et al. [21] have reported in their Fe doped (4–8 at.%) and pure TiO_2 thin films deposited by pulsed laser deposition on Si(111) substrate reveal RTFM hysteresis behavior. Ohtsuki et al. [22] have investigated electronic structures

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of the room temperature ferromagnet Co:TiO_2 anatase films and showed the importance of the charge neutrality condition: $Co^{2+} + V_O^{2-} + 2Ti^{4+} \leftrightarrow Co^{2+} + 2Ti^{3+}$ (V_O is oxygen vacancy), which gives rise to the elusive Ti 3*d* carriers mediating ferromagnetism via the Co 3*d*–O 2*p*–Ti 3*d* exchange interaction pathway of the occupied orbital.

The Co-doped TiO_2 is a promising candidate owing to its excellent optical and magnetic properties. In DMS the localized electrons of the magnetic ions couple with the extended electrons in the semiconducting band. These couplings lead to a number of peculiar and interesting properties such as magneto-optical and magneto-electrical effects and this paper is an effort to explain the nature of these couplings with the room temperature ferromagnetism. In this paper, we have carried out a systematic study of the Co doped TiO_2 polycrystalline samples prepared by solid state reaction method with the help of XRD, Raman Spectroscopy, UV–VIS–NIR Spectroscopy, and Superconducting Quantum Interference Device (SQUID). The results have been explained to show the role of Co-doping on the Structural, optical and magnetic properties to explain the ferromagnetism induced.

2. Experimental details

Polycrystalline samples in the series $Ti_{1-x}Co_xO_2$ (where $x = 0.00$, 0.05 and 0.10) were prepared using the solid-state reaction route. Commercially available high purity TiO_2 (99.99%) and CoO (99.99%) chemical powders from Alfa Aesar were used for sample preparation. In solid-state reaction route of preparation, both chemicals were mixed rigorously with the help of Agate mortar & pestle in stoichiometric proportion. The grinding of the mixtures were carried out rigorously for more than 20 h for each sample and then the powders were annealed for 15 h at 500 C in a microprocessor controlled furnace to obtain the polycrystalline precursors. Then the powder were pressed into Pellets (12 mm diameter and 1 mm thickness) using a hydraulic pressure of nearly 5 tons and sintered at 600 °C in Ar atmosphere.

The crystalline structures of the samples were determined using powder X-ray Diffractometer (Bruker D8 Advance) using Cu K_α radiation as an X-ray source. The scans were taken from 20° to 90° angle range with a step size of 0.01°. As confirmed from our XRD analysis, annealing neither altered the structure nor generated any impurity phase. Raman spectroscopy was further used to check the Raman modes associated with TM-O vibrations, which can change with creation and destruction of oxygen vacancies. As Raman scattering can yield important information about the nature of a solid on a scale of the order of a few lattice constants, it can be used to study the microscopic nature of structural or topologic disorder. The Raman measurements were performed on DeltaNu Advantages series 532 Raman spectrometer connected with a Charge Coupled Device (CCD) detector. Green laser at 532 nm was used as an exciting light source in this spectrometer. In order to eliminate heating effects the output power of laser was kept at 100 mW with 10 s Integration time. Optical absorption spectra were studied using a Perkin–Elmer Lambda 750 UV–VIS–NIR spectrophotometer with pre-aligned Tungsten, Halogen and Deuterium sources. The resolution of the spectrophotometer is 0.17–5.00 nm for UV/Vis and 0.20–20.00 nm for NIR.

Field dependent dc magnetization measurements of the samples were characterized using a Superconducting Quantum Interference Device (SQUID) MPMS XL7. The MPMS XL7 consists of several superconducting parts which are magnets to generate large magnetic fields, a detection coil coupling inductively to the sample, a SQUID sensor connected to the detection coil and a magnetic shield surrounding the SQUID. In this SQUID magnetometer the magnetization can be recorded in a temperature range from 1.9 to 300 K and in external magnetic field of up to ±7.0 Tesla (70,000 G).

3. Results and discussion

3.1. XRD data

Fig. 1(a) displays the best fitted XRD patterns of $Ti_{1-x}Co_xO_2$ (where $x = 0.00$, 0.05 and 0.10), along with the full-profile least-squares refinement fit to the data. All the peaks are well indexed and fitted in the tetragonal anatase phase of TiO_2 (space group: I 41/*a m d* (No. 141), $Z = 4$). The results of the refinement are listed in Table 1. The full pattern Rietveld refinement confirms that TiO_2 crystallizes in the anatase type of tetragonal structure. The obtained values of the lattice parameters for pure TiO_2 are in very good agreement with the anatase structure (Joint Committee for Powder Diffraction Standard, 78-2486) of TiO_2. No other impurity peaks are detected, which ensure high purity of TiO_2 powder used for Co doping. The best fitted XRD patterns for the 5% and 10% Co doped samples recorded at 300 K are also shown in Fig. 1(a). These diffraction patterns do not show any extra peaks confirming that the anatase phase is not disturbed upon Co doping in TiO_2. However, small shifts in Bragg peaks are observed reflecting an expansion of the cell volume as depicted in Fig. 1(b). A significant difference between ionic radii of the dopant and the host ions (i.e. Co^{2+}: 0.745 Å and Ti^{4+}: 0.605 Å, with a coordination number of 6) is expected to cause a small enhancement of the TiO_2 unit cell size. In the refinement process the Co occupancies were varied for

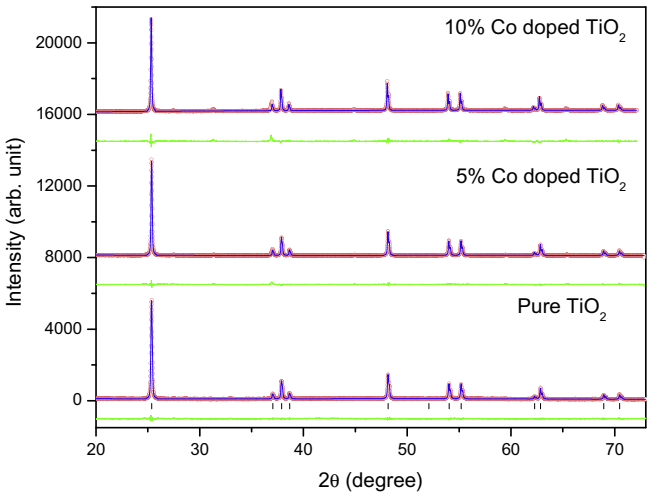

Fig. 1. (a) Fitted XRD patterns of $Ti_{1-x}Co_xO_2$ ($x = 0.00$, 0.05 and 0.10). The observed (calculated) profiles are shown by open circles (solid line) curves. The short vertical marks represent Bragg reflections and the lower curves are the difference (solid line) plot. and (b) best fitted XRD patterns of $Ti_{1-x}Co_xO_2$ ($x = 0.00$, 0.05 and 0.10) in a limited 2θ range, depicting the relative changes in the peak position of the most intense (101) reflection. The observed (calculated) profiles are shown by open circles (solid line) curves. The short vertical marks represent Bragg reflections and the lower curves are the difference (solid line) plot.

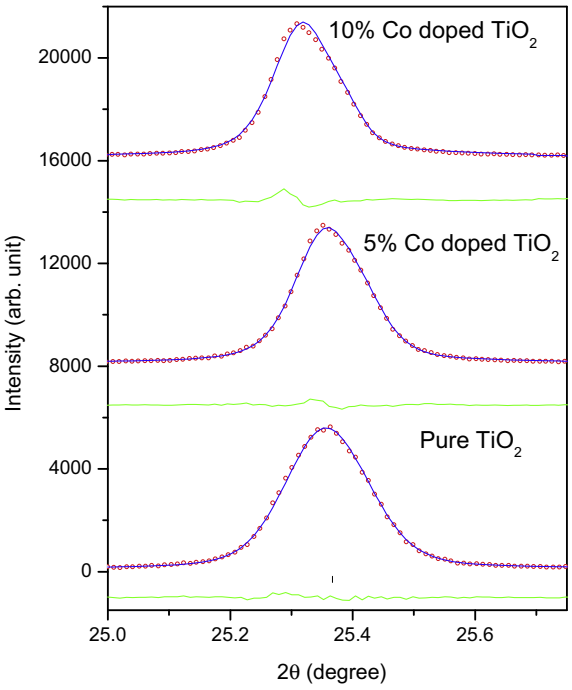

Fig. 1. (*continued*)