

# Effect of Mn doping on structural, optical and magnetic properties of SnO<sub>2</sub> nanoparticles

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**Abstract** The Mn doped SnO<sub>2</sub> nanoparticles synthesized by cost effective chemical co-precipitation method has been investigated in the present work. The main focus of the work is to explore the structural, optical and magnetic properties of the SnO<sub>2</sub> nanostructures. The crystallite size decreases with increase in Mn doping to SnO<sub>2</sub> matrix. The optical band gap of doped SnO<sub>2</sub> nanoparticles continuously decreases with increasing Mn ion doping concentration. All the doped SnO<sub>2</sub> nanoparticles show paramagnetic behavior at room temperature. SnO<sub>2</sub> exhibits ferromagnetic behavior in the range of low external applied magnetic field due to the presence of oxygen vacancies (V<sub>o</sub><sup>+</sup>) and defects. The undoped SnO<sub>2</sub> nanoparticles are spherical in shape while Mn doped SnO<sub>2</sub> nanoparticles show the segregation of the spherically shaped nanoparticles. Mn ions only enhance the paramagnetic ordering and degrade the ferromagnetism already present in the SnO<sub>2</sub> nanoparticle.

## 1 Introduction

The wide-band-gap oxide material has renewed and intensified investigations in recent years due to diverse optoelectronic applications by employing their optical transparency in the visible range. It has been investigated that the oxide films have promising applications such as flat-panel displays, gas sensors, high electrical conductivity, protective coatings, light-emitting devices and spintronics devices etc. [1–10]. Tin oxide (SnO<sub>2</sub>) is known as an n-type wide-band gap (3.6 eV) semiconductor. As an n-type semiconductor, SnO<sub>2</sub> shows very high sensitivity towards reducing gases such as H<sub>2</sub>, CO, hydrocarbon, and alcohol [9–14]. It combines the low electrical resistance with high transparency in visible range and high reflectivity in infra-red range. Tin dioxide (SnO<sub>2</sub>) possesses several unique properties such as transparency, thermal and chemical stabilities resulting into its numerous optoelectronic applications etc. [3–7]. The optical properties of nanocrystalline semiconductors have been studied extensively in recent years for translating their enhanced properties into practical applications. As the size of the material becomes smaller, it changes the band gap and becomes larger thereby changing the optical and electrical properties of the material and making the material suitable for new applications and devices. Tailoring the physical properties and adding new functionalities to the existing semiconductors by altering the composition, structure, morphology and grain/particle size are the new approaches in advancing the current applications of semiconductor materials. The preparation of such materials in the nanosized range helps in getting increased surface-to-volume ratio which might affect the structural and most other physical properties. The optoelectronic properties such as photoluminescence and optical band gap of SnO<sub>2</sub> can also be improved by impurity

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doping. The researchers have shown that several dopants (Co, Fe and Cu) can lead to an increase of surface area of SnO<sub>2</sub> by reducing the grain size and crystallinity [15–17]. Various approaches have been adopted for the synthesis of SnO<sub>2</sub> nanoparticles including the hydrothermal method [18, 19], solvothermal method [20], gel-combustion and sol–gel method [21, 22]. Among all these routes the co-precipitation method is an effective way to control the topography and surface properties of metal oxides. In this work the effect of Mn doping on the structural, magnetic and optical properties of SnO<sub>2</sub> nanoparticles prepared by co-precipitation method have been investigated.

## 2 Experimental procedure

The Mn doped SnO<sub>2</sub> nanocrystalline materials were prepared by the chemical co-precipitation method. All the chemical reagents were used of AR grade and used directly without further purification. In typical synthesis of SnO<sub>2</sub> the stannic tetrachloride hydrated (SnCl<sub>4</sub>·5H<sub>2</sub>O); 3.5058 g was dissolved in 100 mL distilled water to prepare 0.1 M solution under vigorous magnetic stirring for 30 min at room temperature. The 4 mL of aqueous ammonia solution was added to the above solution drop wise under stirring to maintain pH in the range of 7–8. The dropping of the solution was well controlled for the chemical homogeneity of the samples. After ageing of 20 h the slurry was filtered and washed around 10 h with distill water to remove impurities from the precipitate. This precipitate was dried in an oven at 70 °C for 10 h to remove water molecules and then calcinated at 400 °C for 2 h in furnace. The calcinations process was started at room temperature. After calcinations the samples were crushed into fine powder to get tin oxide nanomaterials.

For the synthesis of Mn doped SnO<sub>2</sub>, the stannic tetrachloride hydrated (SnCl<sub>4</sub>·5H<sub>2</sub>O), 3.5058 g and manganese (II) acetate (IV) hydrate crystal [(CH<sub>3</sub>COO)<sub>2</sub> Mn·4H<sub>2</sub>O], 0.0245 g (1 at.%) was taken to dissolve in 100 mL distilled water to prepare 0.1 M solution under vigorous magnetic stirring for 30 min. An ammonia solution was added drop wise in this solution under stirring to maintain the pH in between 7 and 8. This process was repeated for 3 at.% (0.0735 g), 5 at.% (0.1225 g), 7 at.% (0.1715 g) and 10 at.% (0.2451 g) of Mn doping. After ageing of 20 h the slurry was filtered and washed out for 10 h with distilled water to remove impurities from the precipitate. This precipitate was then dried in an oven at 70 °C for 10 h to remove water molecules and then calcinated at 400 °C for 2 h in a furnace. The samples were crushed after calcinations into fine powder to get Mn doped tin oxide nanomaterials of different doping concentration. Figure 1 shows

the flow chart for the synthesis of Mn doped SnO<sub>2</sub> nanoparticles.

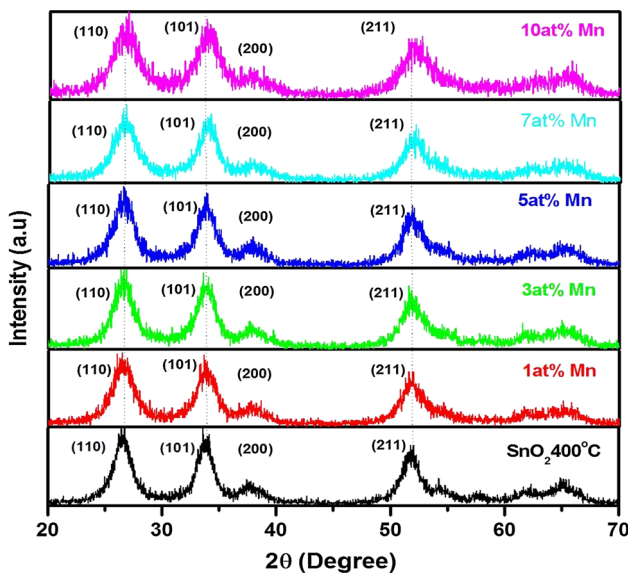
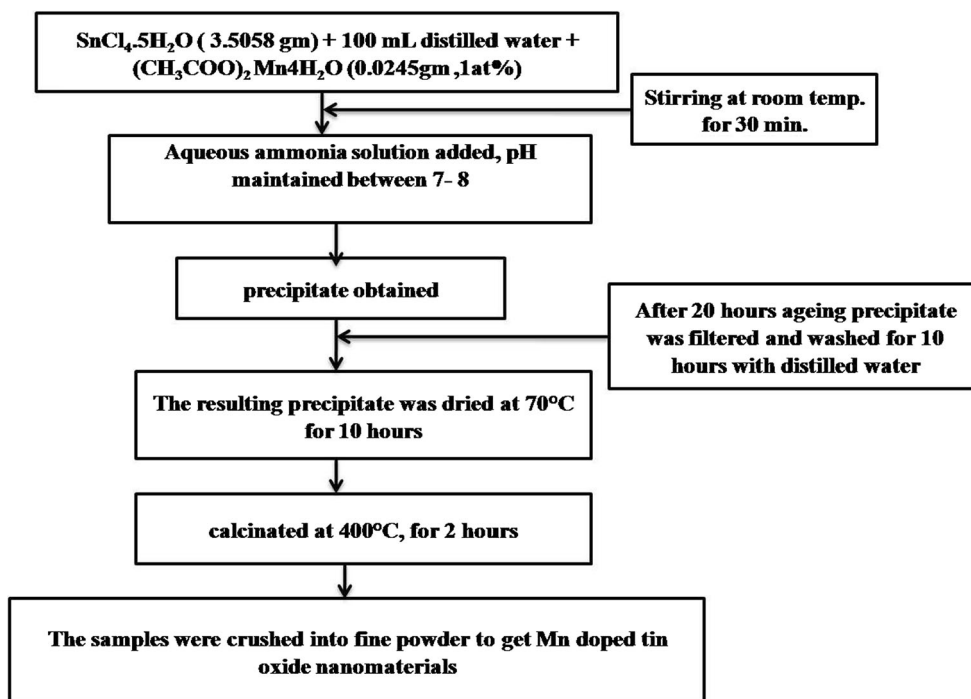
The structural properties of synthesized undoped and Mn doped SnO<sub>2</sub> powder samples were analysed by X-ray diffraction (XRD) measurements using powder diffractometer (Bruker AXS D8) with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The size and shape of the synthesized powder were studied by Transmission Electron Microscopy (TEM) measurements using TEM (Hitachi- H-8100). The Fourier Transform Infrared Spectroscopy (FT-IR) spectra of the synthesized samples have been recorded in the spectral range 500–4000 cm<sup>-1</sup> with Perkin-Elmer 1600 Fourier transform instrument using the KBr pellet technique. The absorption spectra of the samples are taken for the spectral range 250–800 nm with Perkin-Elmer Lambda 35 Ultraviolet Visible (UV–vis) spectrophotometer. The room temperature Raman Spectroscopy (RS) of the powder samples were recorded in the spectra range, 100–1100 cm<sup>-1</sup> using Thermo Scientific DXR-XI Raman Imaging Microscope. The 532 nm laser line of the Ar<sup>+</sup> ions laser was used to illuminate the powder samples. The photoluminescence emission spectra of the synthesized samples were recorded by using a Spectro-fluorometer (Spex Fluorolog3, FL3-22) with a 450 W Xenon Lamp as the excitation source with 330 nm excitation wavelength. For recording the PL spectra, emission slit width was kept to 3.0 nm. The room temperature magnetic properties of the synthesized samples were measured by Vibrating Sample Magnetometer (VSM) (Microsense EV7) measurements.

## 3 Results and discussion

### 3.1 X-ray diffraction

Figure 2 represents the powder XRD pattern of pure and 1, 3, 5, 7 and 10 at.% of Mn-doped SnO<sub>2</sub> nanocrystals. Peaks with intensity corresponding to (110), (101) and (211) planes are observed, which indicates that the sample is of high purity with cassiterite SnO<sub>2</sub> structure (JCPDS No. 41-1445). It is clear that there are no extra peaks due to Mn metal oxide implying that the transition metal ion gets substituted at the Sn site without changing the structure. The Table 1 illustrates that the crystallite size reduces from 5.6 to 3.1 nm for doped SnO<sub>2</sub> nanoparticles. It is revealed that as the Mn doping concentration increases from 1 % to 10 at.% the presence of Mn ions in SnO<sub>2</sub> prevented the growth of crystal grains. This suggest that Mn ions are incorporate into the lattice in the form of Mn<sup>3+</sup> (radius 0.065 nm) or Mn<sup>4+</sup> (radius 0.054 nm), as the ionic radius of Mn in these two states is smaller than the ionic radii of Sn<sup>4+</sup> (0.070 nm) [23].

**Fig. 1** Flow chart for synthesis of Mn doped SnO<sub>2</sub> nanoparticles



**Fig. 2** XRD of the samples calcinated at 400 °C

There is an increase in crystallinity in the Mn doped metal oxide SnO<sub>2</sub> nanoparticles when compared to the pure SnO<sub>2</sub> nanoparticles. This physical process suggest that a portion of the metal oxide ions forms stable solid solution with SnO<sub>2</sub> and the metal oxide ions occupy the regular lattice site in SnO<sub>2</sub>. This will introduce the point defects and change in stoichiometry owing the charge imbalance, which may induce the distortion in crystal structure of the host compound. If metal ions occupy the regular lattice site in SnO<sub>2</sub>, then the interference takes place between Mn-

doped metal ions and those of SnO<sub>2</sub> lattice and thus the crystallinity of the doped nanoparticles tends to enhance than that of pure SnO<sub>2</sub> nanoparticles.

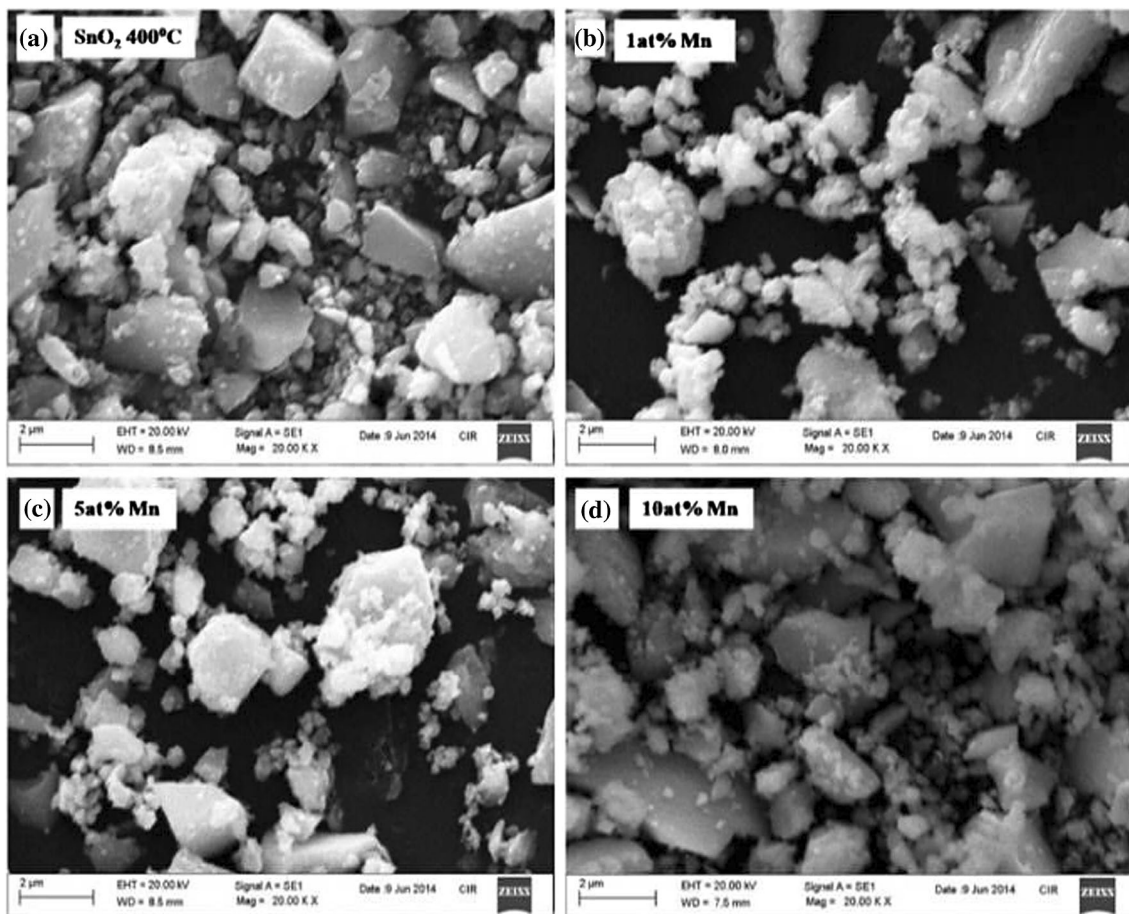
### 3.2 Scanning electron microscope and transmission electron microscope

Figure 3 shows the overall surface morphology of pure and doped SnO<sub>2</sub> nanoparticles. It is observed from that pure SnO<sub>2</sub> compound consists of large agglomeration than doped SnO<sub>2</sub>. The SEM investigations of all the samples reveal the crystallites nature of nanoparticles. The TEM images are depicted in Figs. 4, 5 and 6 which illustrates that the nanoparticles are spherical in shape. The doped SnO<sub>2</sub> shows clusteration of spherically shaped nanoparticles. The selected area electron diffraction (SAED) indicates that polycrystalline nature of the samples. It shows that the crystallinity increases with increase in Mn content.

The interplanar spacing calculated for different sets of planes is approximately same as for the main peaks observed in the XRD pattern. The estimated d-spacing for (110) plane is 0.335 nm. The average particle size was calculated from particle size distribution curve shown in Fig. 7a–c. The calculated average particle size is 7.8 ± 0.3, 6.3 ± 0.4 and 7.5 ± 0.4 nm for undoped SnO<sub>2</sub>, 1 and 5 at.% Mn doped SnO<sub>2</sub> nanoparticles respectively. Particle size calculated from TEM images is comparable with the calculated crystallite size from the XRD. In general the particles observed from TEM images are likely to contain a single or several primary crystallite grains which

**Table 1** Lattice parameters and crystallite size of the samples

S. No.	Samples	Lattice parameter (Å)	Average crystallite size (nm)
1	SnO <sub>2</sub> 400 °C	a = b = 4.784 c = 3.211	5.6
2	1 at.% Mn	a = b = 4.806 c = 3.223	4.9
3	3 at.% Mn	a = b = 4.699 c = 3.204	3.7
4	5 at.% Mn	a = b = 4.780 c = 3.178	3.6
5	7 at.% Mn	a = b = 4.682 c = 3.253	3.2
6	10 at.% Mn	a = b = 4.646	3.1



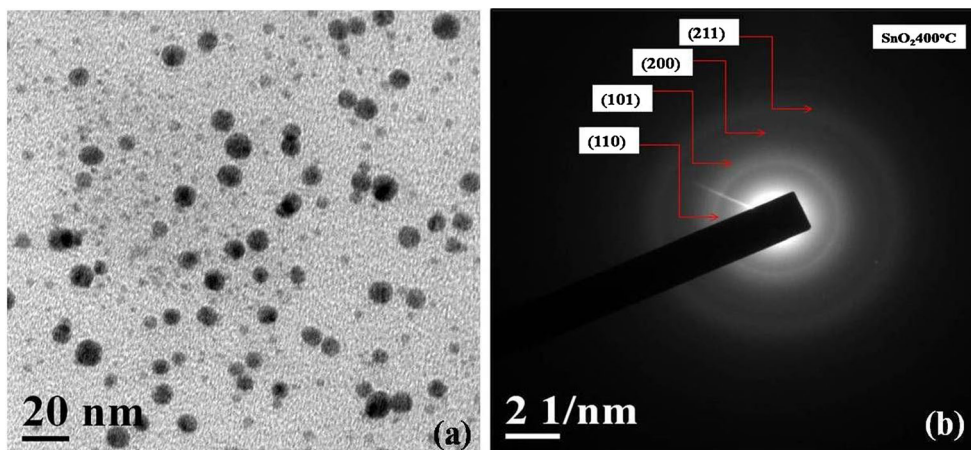
**Fig. 3** SEM images of Mn-doped SnO<sub>2</sub> nanoparticles at 2 μm scale are measured in terms of average mean crystallite size by XRD.

### 3.3 Optical properties

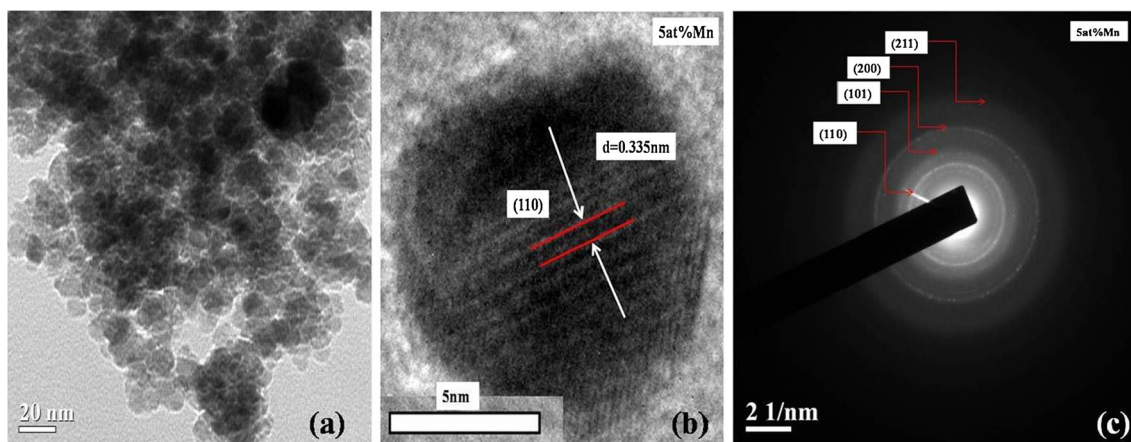
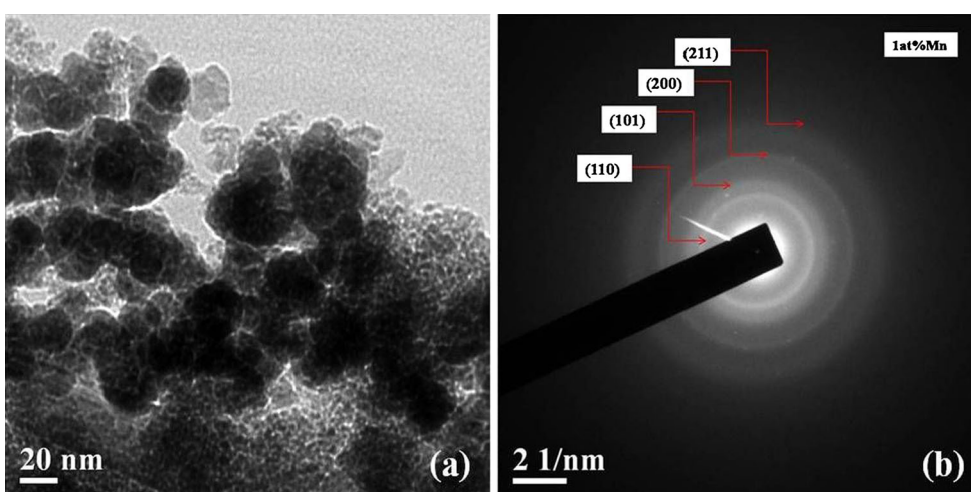
Absorption and fluorescence spectroscopy are powerful nondestructive techniques to explore the optical properties of semiconducting nanoparticles. In order to determine the

optical band gaps and associated properties, the optical absorbance measurement were carried out at room temperature and the absorbance of pure and Mn doped SnO<sub>2</sub> nanoparticles are shown in Fig. 8. The absorbance is expected to depend on several factors such as band gap, impurity centers, vacancies and surface roughness [24]. Absorbance spectra exhibit an absorption peak at around 280 nm which can be attributed to the photo excitation of

**Fig. 4** **a** TEM image and **b** SAED pattern of un-doped SnO<sub>2</sub>



**Fig. 5** 1 at.% Mn-doped SnO<sub>2</sub> **a** TEM image and **b** SAED pattern



**Fig. 6** 5 at.% Mn-doped SnO<sub>2</sub> **a** TEM image, **b** HRTEM image and **c** SAED pattern

electrons from valence band to conduction band. The absorption edge of different samples varies as the concentration of Mn doping in the SnO<sub>2</sub> nanoparticles. It can be seen that the absorbance tends to increase with the increase in dopant concentration.

Tauc plots as shown in Fig. 9 were used to calculate the direct band gap by using the Tauc relation:

$$\alpha h\nu = A(h\nu - E_g)^n$$

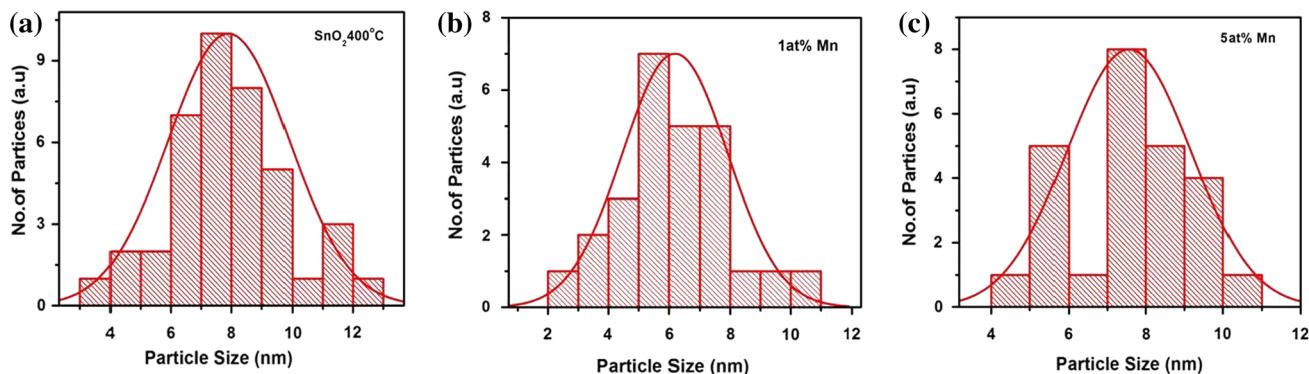


Fig. 7 Particle size distribution curve; a  $\text{SnO}_2$ , b 1 at.% Mn doped  $\text{SnO}_2$  and c 5 at.% Mn doped  $\text{SnO}_2$

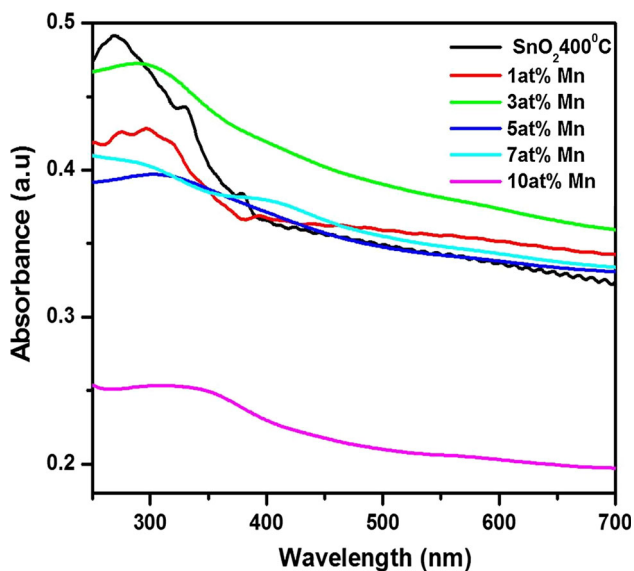


Fig. 8 Optical absorption spectra of the samples

where  $\alpha$  is the absorption coefficient,  $A$  is a constant.  $n = 1/2$  for direct band gap semiconductors. The linear region in the plot of  $(\alpha h\nu)^2$  versus  $h\nu$  can be extrapolated to calculate the value of the optical band gap  $E_g$ . The measured band gap was found to be 2.81 eV for undoped  $\text{SnO}_2$  nanoparticles (Table 2), which is lower than the reported value of the bulk  $\text{SnO}_2$  (3.6 eV). The spectra of Mn doped  $\text{SnO}_2$  nanoparticles display red shift in the band gap with increasing the dopants amount. The similar shift was observed by other researcher by incorporation of metal ions into  $\text{SnO}_2$  nanoparticles [25–27]. This Red shift can be assigned to the charge-transfer transitions between the metal ions d-electrons and the  $\text{SnO}_2$  conduction or valence band [28].

### 3.4 FT-IR analysis

FT-IR spectra of the samples are shown in the Fig. 10. It is observed that there are clear changes in the positions and

sizes of IR peaks indicating that Mn has incorporated into  $\text{SnO}_2$  host matrix. The band observed at  $670\text{ cm}^{-1}$  may be assigned to the antisymmetric Sn–O–Sn stretching mode. The band in the region  $480\text{--}510\text{ cm}^{-1}$  can be attributed to symmetric Sn–O–Sn and Mn–O bonds. The peak appearing at  $1120\text{ cm}^{-1}$  is related to the vibration of hydroxyl-tin (Sn–OH) bond. The vibration band observed at  $1380\text{ cm}^{-1}$  can be assigned to N–O symmetric stretch for the existence of nitro based compounds due to synthesis from nitrates precursors in the samples while the peak at  $1694\text{ cm}^{-1}$  is assigned to C=O stretching vibration. The present assignments corroborate well with the values reported in available literature [29, 30]. The prominent bands around  $3800$  and  $1630\text{ cm}^{-1}$  account for the presence of absorbed molecular water.

### 3.5 Photoluminescence

Photoluminescence (PL) is a useful tool for investigating the optical properties of undoped and doped semiconductor nanostructures. The doped nanostructures are expected to have different optical properties in comparison to undoped nanostructures. Figure 11 shows the photoluminescence (PL) spectra of undoped and Mn doped  $\text{SnO}_2$  nanoparticles. The PL spectra of the synthesized samples are obtained as a result of the competition among electron–hole separations, electron–phonon scattering and electron–hole recombination. The band edge emissions centered in the range of  $393\text{--}396\text{ nm}$  can be attributed to the  $V_o$  related defects, mainly singly ionized oxygen vacancy ( $F^+$  center or  $V_o^+$ ) defects which are believed to be recombination of excitons for all the samples [31]. The PL spectra exhibits a broad emission edge in the range of  $400\text{--}500\text{ nm}$  which is the indication for the presence of multiple peaks under a main peak corresponding to multiple emissions from oxygen vacancies present in these samples. These vacancies thus generates the defect levels in the crystal and enhances the visible emission in the spectra [24, 32].

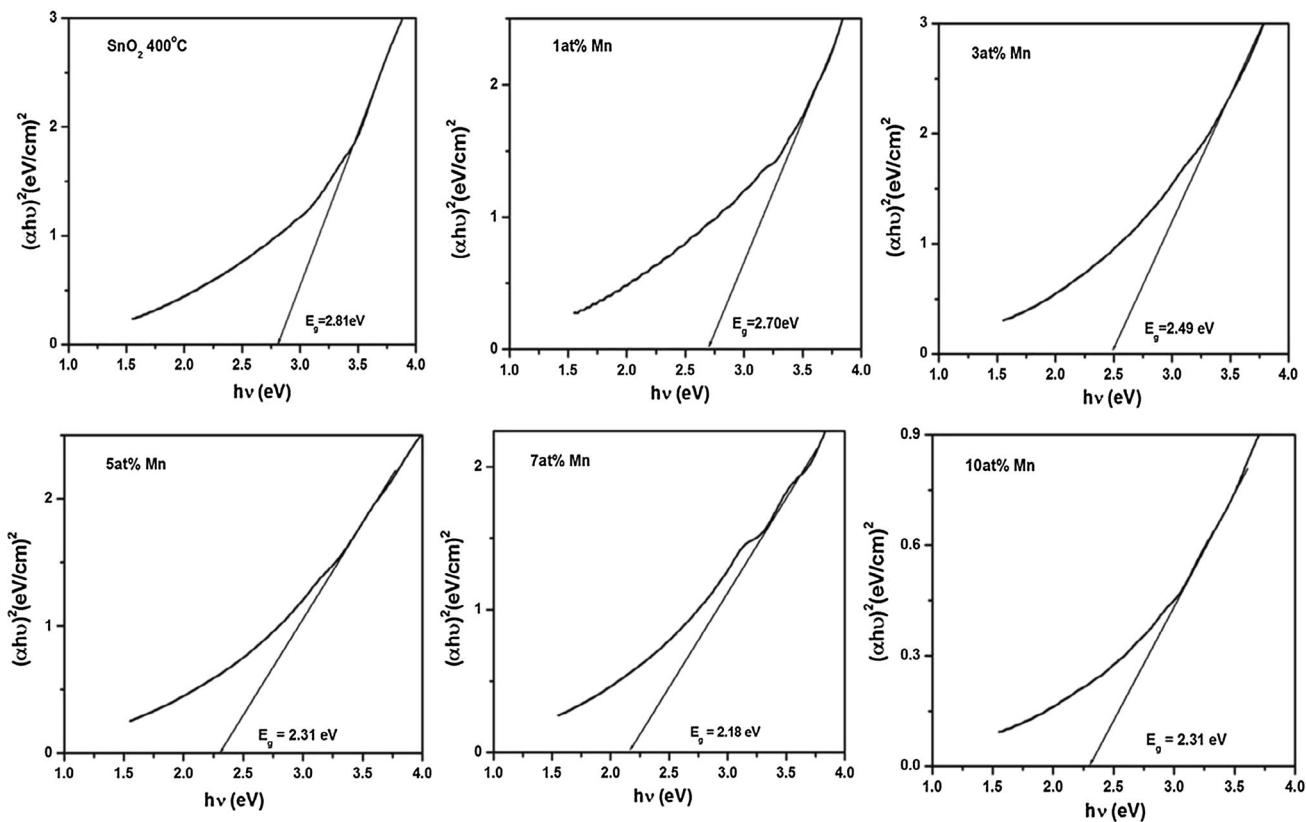


Fig. 9 Tauc plot of the samples

Table 2 Absorption edges and energy band gap of all the samples

Mn concentration (at.%)	Wavelength (nm)	Energy band gap (eV)
0	441	2.81
1	460	2.70
3	498	2.49
5	537	2.31
7	569	2.18
10	537	2.31

### 3.6 Raman spectra

Figure 12 shows the Raman spectra for undoped and Mn doped SnO<sub>2</sub> nanoparticles within the range 100–1100 cm<sup>-1</sup>. SnO<sub>2</sub> having tetragonal rutile crystalline structure with point group *D*<sub>4h</sub><sup>14</sup> and space group *P4*<sub>2</sub>/*mnm* consist of the six unit cell atoms which give a total of 18 branches for the vibration modes in the first Brillouin’s zone. The representation of the vibration modes at the center of the Brillouin’s zone is given as [33]:

$$\Gamma = 1A_{1g} + 1A_{2g} + 1A_{2u} + B_{1g} + 1B_{2g} + 2B_{1u} + 1E_g + 3E_u$$

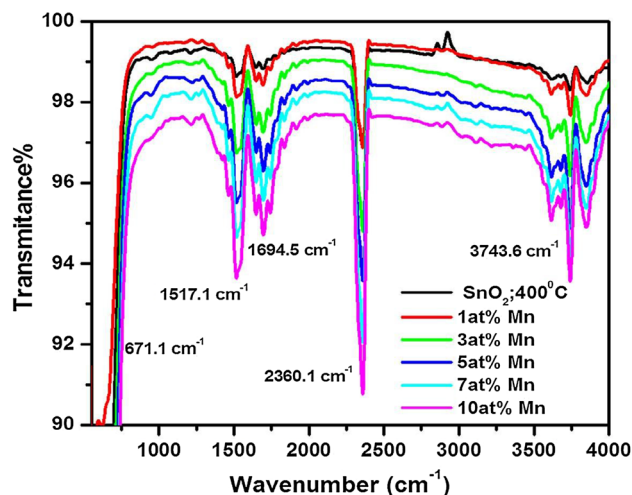


Fig. 10 FT-IR spectra of SnO<sub>2</sub> and Mn doped SnO<sub>2</sub> samples

where the *B*<sub>1g</sub>, *E*<sub>g</sub>, *A*<sub>1g</sub>, and *B*<sub>2g</sub> modes of SnO<sub>2</sub> are Raman active. Here *E*<sub>u</sub> and *A*<sub>2u</sub> bands are infrared (IR) active, and *A*<sub>2g</sub> and *B*<sub>1u</sub> are silent or inactive to both Raman and IR. One *A*<sub>2u</sub> and two *E*<sub>u</sub> modes are acoustic. In the Raman active modes Sn atoms remain at rest while oxygen atoms

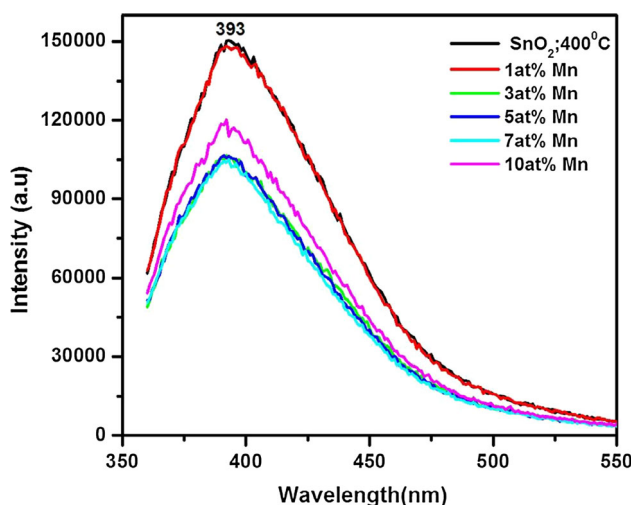


Fig. 11 PL spectra of all the samples

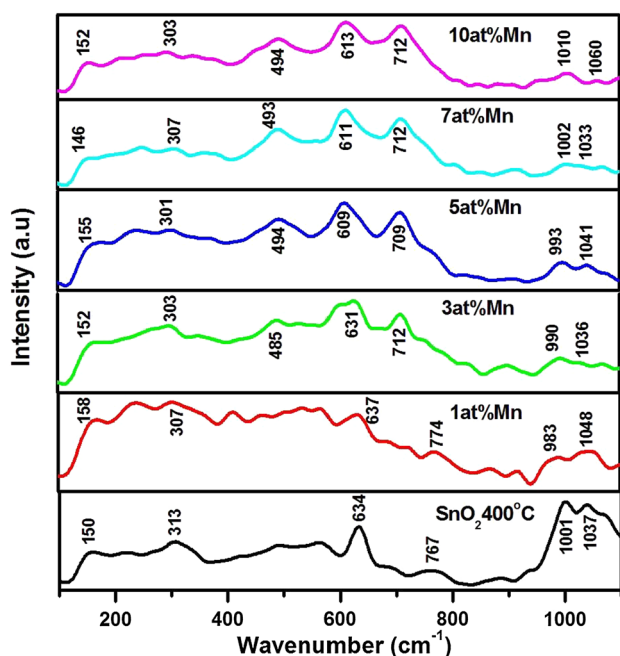


Fig. 12 Raman spectra of all the samples

vibrate. The Raman bands of the pure rutile phase  $\text{SnO}_2$  were observed in different range of the Raman spectra. The broad band centered in the range of  $485\text{--}494\text{ cm}^{-1}$  for all the samples is assigned to  $E_g$  band. The vibrational band in the range of  $609\text{--}637\text{ cm}^{-1}$  is the most fundamental mode of vibration of rutile phase of  $\text{SnO}_2$  and assigned to  $A_{1g}$ . The third fundamental mode of vibration for undoped and 1 at.% doped  $\text{SnO}_2$  is found in the range of  $767\text{--}774\text{ cm}^{-1}$  and is attributed to  $B_{2g}$ . The  $A_{1g}$  and  $B_{2g}$  modes are non degenerate and might be related to the expansion and contraction of the vibrating mode of Sn–O bonds, whereas the doubly degenerate  $E_g$  mode may be related to the

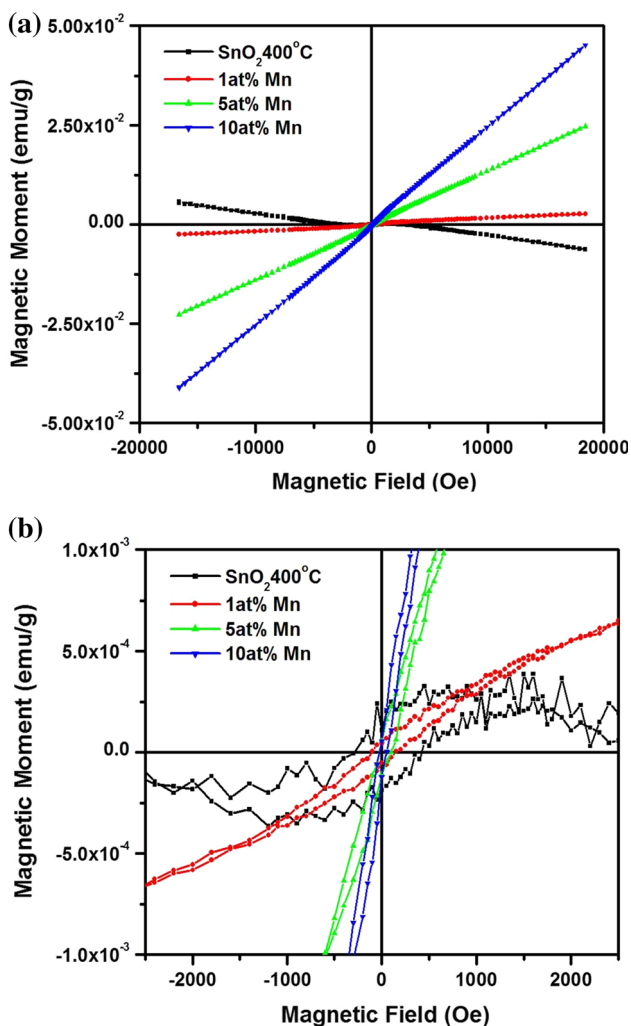
vibration of oxygen in the oxygen plane. The  $B_{2g}$  and  $A_{1g}$  modes present in the spectra vibrate in the plane perpendicular to the  $c$ -axis, while the  $E_g$  mode always vibrates in the direction of the  $c$ -axis. The gradual changes in the Raman spectra has been observed with the increase of 3 at.% Mn doping in the  $\text{SnO}_2$  lattice which may be attributed to the strong electron–phonon interaction in the system. Few new Raman bands in the low wavenumber region ( $140\text{--}315\text{ cm}^{-1}$ ) with a very low intensity can be observed in most of the samples which are associated with the surface modes of  $\text{SnO}_2$  nanostructures. Additional peaks in the range of  $983\text{--}1060\text{ cm}^{-1}$  can be observed in all the samples, which can be assigned to laser-excited luminescence due to presence of defects in  $\text{SnO}_2$  nanoparticles [32–34].

### 3.7 Magnetic properties

The field dependent magnetization [ $M(H)$  at 300 K] measurement of  $\text{SnO}_2$  and Mn (1, 5 and 10 at.%) doped  $\text{SnO}_2$  nanocrystalline samples calcinated at  $400\text{ }^\circ\text{C}$  are shown in Fig. 13. The graph is magnified in the central region (in the region  $-2500$  to  $2500$  Oe) and is shown in Fig. 13b. All the measurements shown here have been corrected by eliminating the signals from the sample holder. All curves clearly exhibit hysteresis behavior and magnetization under a strong externally applied magnetic field of 20 KOe. The Mn (1, 5 and 10 at.%) doped  $\text{SnO}_2$  graph exhibits paramagnetism at room temperature under an externally applied magnetic field of 20,000 Oe. The undoped  $\text{SnO}_2$  nanoparticles exhibit ferromagnetism with low coercivity and positive susceptibility only for externally applied lower magnetic field region of  $-2500$  to  $2500$  Oe. The maximum coercivity ( $\sim 450$  Oe) was observed for undoped  $\text{SnO}_2$  which decreases gradually for Mn doped  $\text{SnO}_2$  nanocrystalline samples.

The  $\text{SnO}_2$  nanoparticles exhibit diamagnetic behavior for an externally applied magnetic field of higher than 2500 Oe. The coercivity and positive susceptibility may be associated with the exchange coupling of the spins of electrons trapped in oxygen vacancies ( $V_o$ ), which are mainly present on the surface of the  $\text{SnO}_2$  nanoparticles and the surface defects created during synthesis process as evident from PL spectra also. The literature reveals that these oxygen vacancies basically located on the particle surface are considered to play a key role for the paramagnetism and ferromagnetism in nanosized  $\text{SnO}_2$  [35–41]. Unpaired electrons can be trapped in those oxygen vacancies and their spins can polarize together via exchange interactions and lead to ferromagnetic order in  $\text{SnO}_2$  nanoparticles [35]. As the strength of externally applied magnetic field is increased the magnetic susceptibility continuously increases for Mn doped  $\text{SnO}_2$





**Fig. 13** **a** M–H plot of SnO<sub>2</sub> and Mn doped (1, 5 and 10 at.%) SnO<sub>2</sub> nanoparticles and **b** magnified graph

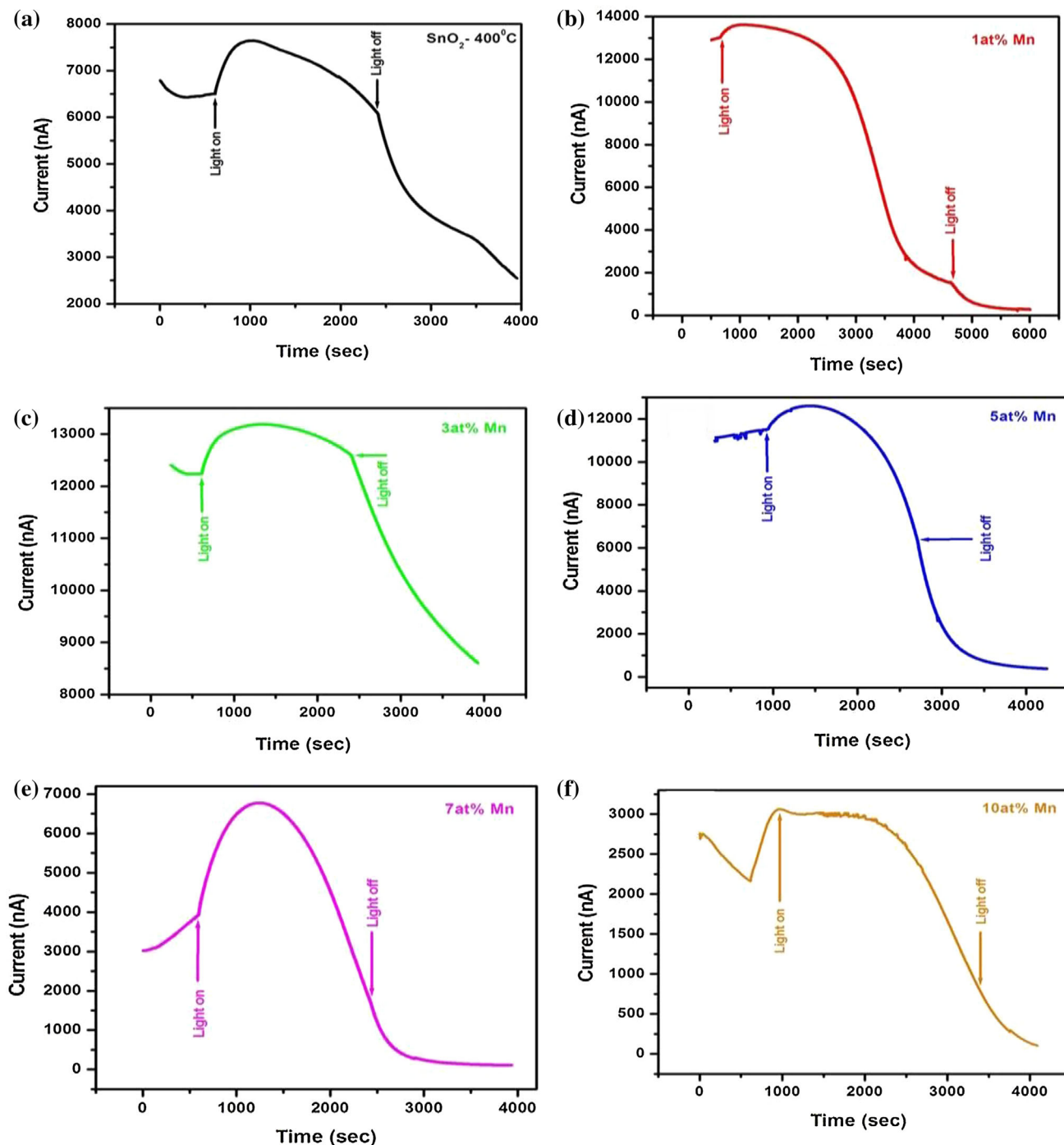
nanoparticles and consequently the graphs show paramagnetic nature for all the doped samples. The similar existence of paramagnetic and ferromagnetic moments has been reported previously by other researchers in pure and doped SnO<sub>2</sub> [32, 35–42]. The graphs illustrate that as the Mn dopant concentration increases the particles become more aligned in the direction of applied magnetic field as the net magnetic moment increases after Mn doping. These results strongly suggest that the magnetic order observed in the Mn-doped SnO<sub>2</sub> nanoparticles is intrinsic in nature. Therefore, the main role of the Mn cations is not to originate the magnetic ordering; rather, it only modifies the paramagnetism and degrades the ferromagnetism already present in the SnO<sub>2</sub> nanoparticles. Besides this, the presence of extrinsic impurities or paramagnetic phases with concentrations well below the detection limit of the instruments can be responsible for the enhanced paramagnetic signals observed at room temperature [39–42]. Further investigations are required to understand such room

temperature magnetic behavior of undoped and doped SnO<sub>2</sub> based DMS nanostructures. Magnetic and optical properties of different RE and transition metals (TM's) doped SnO<sub>2</sub> nanoparticles of different particle shape and sizes are currently under study and will be published elsewhere in the future.

### 3.8 Time resolved photoconductivity rise and decay measurement

The time-resolved rise and decay photocurrent spectrum helps in understanding the photoconductivity dynamics of materials when the light is abruptly switched on and off. The rise and decay of photocurrent spectrum can be useful in determining the nature of recombination centers present inside the materials. The time-resolved rise and decay at room temperature for the photocurrent spectrum of the undoped and doped SnO<sub>2</sub> nanoparticles under visible illumination of 370 nm are shown in Fig. 14. The prepared SnO<sub>2</sub> nanoparticles are n-type semiconductors due to oxygen vacancies and other native defects. Such vacancies and defects serve as active sites for the adsorption of oxygen and H<sub>2</sub>O molecules. The surface-related mechanism, which is governed by desorption and adsorption processes, plays an important role in the photoconductivity properties of the nanostructures due to their large surface-to-volume ratio [43]. The graph shows that when the field is applied, the initial dark current is high in most of the samples. This is attributed to the presence of oxygen vacancies at the surface and other native defects acting as donors, as well as the process of adsorption of water molecules, thus releasing the charge carriers. Thereafter, the dark current starts decreasing and attains its minimum value. The reduction in the dark current is rapid in SnO<sub>2</sub> as compared to the doped SnO<sub>2</sub> nanoparticles. The anomalous behavior in time-resolved photoconductivity may be attributed to the presence of an additional hydroxyl group, as generally the decrease in conductivity is due to the field-induced adsorption of oxygen from air [44]. As the illumination of light is switched off, electron–hole recombination process dominates, so the conductivity decreases in all the samples. The trap depth value was calculated to be 0.69, 0.68, 0.66, 0.65, 0.67 and 0.66 eV for pure and 1, 3, 5, 7 and 10 at.% of Mn-doped SnO<sub>2</sub> nanoparticles, respectively [31]. Trap depth is maximum for the undoped sample, indicating that higher energy is required to remove an atom from the trap as compared to the other samples.

Kumar et al. [45] have reported the growth and decay of the photocurrent generation in Cu–Ni nanoparticle-decorated r-graphene hybrid nano-composite (Cu–Ni GrHNC). In their study, they also observed similar results that initially the increase in photocurrent is very fast with a time



**Fig. 14** Time resolved rise and decay photoconductivity measurement for the samples

constant of 0.84 s, and then growth becomes slow with a time constant of 31.73 s and finally it gets saturated. As the power is switched off, a fast decay in the current with decay time constant of 2.2 s was observed, which further keep decreasing with a slower decay time constant of 93.19 s. In our case the growth and decay time constants are slow as compared to Kumar et al. results. These slow

photoconductive rise and decay response may be attributed to a large amount of recombination centers and presence of trap levels and defect states within the band gap [46, 47]. Srivastava et al. [46] reported the similar photo response properties for variation in Cu dopant concentration on ZnS nanoparticles synthesized by co-precipitation method. The photocurrent initially found to increase in all Cu doped ZnS

samples due to fast process of generation of electron–hole pairs (EHPs) as a result of absorption of photons. For the un-doped (ZnS) sample, photocurrent increases up to maximum value and then starts decreasing slowly even during illumination. Such kind of negative photoconductivity (NPC) is caused by the presence of imperfection centers in the forbidden gap as observed in our case also [46]. Maurya et al. [47] reported the photoconducting behavior in rutile TiO<sub>2</sub> synthesized by simple hydrolysis method at low calcination temperatures of 80 and 450 °C. The observed trap depth value in their case was 0.65 and 0.69 eV for TiO<sub>2</sub> samples calcinated at 80 and 450 °C respectively. These results are in good agreements with the trap depth value calculated in our case for Mn doped SnO<sub>2</sub> nanoparticles.

#### 4 Conclusion

Mn doped SnO<sub>2</sub> nanoparticles were synthesized by a simple chemical co-precipitation method. The rutile phase tetragonal crystal structure of doped SnO<sub>2</sub> nanostructures was confirmed from XRD, HRTEM and SAED analysis. Crystallite size decreases with increase in Mn doping concentration in SnO<sub>2</sub> nanostructures. The SnO<sub>2</sub> nanoparticles are spherical in shape while the doped SnO<sub>2</sub> crystallites show clusteration of spherically shaped nanoparticles. The optical band gap of undoped SnO<sub>2</sub> nanoparticles was calculated to be 2.81 eV and it decreases continuously with the increase of Mn doping in SnO<sub>2</sub>. The room temperature ferromagnetism in SnO<sub>2</sub> nanoparticles due to the presence of defects and oxygen vacancies has been observed while the Mn doped SnO<sub>2</sub> nanoparticles exhibit room temperature paramagnetism. The strong optical absorption with weak magnetic properties at room temperature may serve the nanomaterials as a potential candidate for many spintronics, optoelectronics and DMS based applications.

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