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Luminescence properties of $Sn_{1-x}Fe_xO_2$ nanoparticles

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Abstract: Nanoparticles of $Sn_{1-x}Fe_xO_2$ ($x = 0$, 0.02, 0.05, 0.1) have been prepared by co-precipitation method using $SnCl_2$ and $FeSO_4$ precursors and subsequent heat-treatment at 600°C. X-ray Diffraction (XRD) study shows that these nanoparticles crystallise in tetragonal system. The unit cell volume increases slightly with Fe^{2+} doping indicating substitution of Sn^{4+} sites by Fe^{2+} ions. The unit cell volume increases from 72.24 $Å^3$ to 72.90 $Å^3$ as x varies from 0 to 0.1. With increasing Fe^{2+} concentration, the peaks in X-ray diffraction pattern become broad because of strain effect produced from substitution of smaller ionic radius Sn^{4+} (0.69 Å) by large one Fe^{2+} (0.77 Å). The average crystallite size was found to decrease from 21 nm to 11 nm as x changed from 0 to 0.1. In Transmission Electron Microscopy (TEM) study of pure SnO_2, the particles are spherical in shape and particle size is found to be 25 nm, which is close to 21 nm from XRD study. Its Selected Area Electron Diffraction (SAED) confirms the tetragonal system. In infrared study, a broad peak centred around 650 cm^{-1} was observed due to Sn-O/Fe-O vibration. From steady state luminescence study, it is found that pure SnO_2 and Fe^{2+} doped SnO_2 show the band-edge emission around 400 nm and the emission intensity decreases with increasing Fe^{2+} concentration. The band-edge absorption occurs in 300–350 nm.

Keywords: nanoparticles; luminescence; band-edge emission.

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1 Introduction

High-transparency semiconductors such as SnO_2 and In_2O_3 have potential applications in flat panel displays and gas sensors, etc. [1–7]. Particularly, bulk SnO_2 has wide band-gap (E_g) of 3.6 eV and thin films can have high conductivity depending on oxygen vacancy [5]. SnO_2 has been synthesised by different methods such as the sol–gel method [8], chemical vapour deposition (CVD) [9], magnetron sputtering [10] and hydrothermal treatment [11]. The electrical conductivity and luminescence properties of SnO_2 are mainly decided by the oxygen vacancy present in SnO_2 lattice [12].

In order to induce room temperature ferromagnetism in non-magnetic semiconductors such as ZnO, SnO_2, etc., doping with transition metals (Mn, Fe, Co, Ni) has been tried in the last few years. This kind of materials, called dilute magnetic semiconductors (DMS), is of great interest as potential materials for spintronic applications [13–15]. Results have been reported on Co, Fe, Ni or Mn doped TiO_2 [13] and SnO_2 systems [14]. In these studies, behaviour of magnetism whether antiferromagnetism or ferromagnetism is highly dependent on the presence of oxygen vacancies. Recently, Punnoose et al. [15] reported that SnO_2 doping with Fe by chemical method leads to ferromagnetism with a Curie temperature of 850 K. To authors' knowledge, there are not many reports about the luminescence properties of Fe doped SnO_2 nanoparticles in the literature. By doping Fe^{2+} in SnO_2, it may introduce oxygen vacancy or trap level within band gap of SnO_2. Also, since particles are in nanosized range, surface/volume atom ratio is large. This may alter luminescence properties of pure SnO_2 and Fe^{2+} doped SnO_2 nanoparticles.

In this manuscript, we have synthesised Fe^{2+} doped SnO_2 nanoparticles by co-precipitation method using stannous chloride and ferrous sulphate as a precursor, ammonia solution as a precipitating agent and carbon black powder as reducing agent. With this method, we can prepare SnO_2 nanoparticles in large amount with low cost precursors. Luminescence properties of Fe doped SnO_2 particles are discussed.

2 Experimental

2.1 Materials

All chemicals used in the experiment are analytic reagent grade. Stannous chloride ($SnCl_2 \cdot 2H_2O$) is purchased from Glaxo SmithKline Pharmaceutical Ltd. Ammonia solution (25%), iron (II) sulphate heptahydrate GR and carbon black powder are purchased from Merck, India. All chemicals are used as received without further purification. Deionised water is used during the reaction.

In typical preparation of $Sn_{1-x}Fe_xO_2$ ($x = 0.02$), 2 g of stannous chloride dihydrate and 0.05 g iron sulphate are dissolved in 100 ml water. After complete dissolution, about 4 ml ammonia solution is added to above aqueous solution with stirring. Stirring is continued for 20 min. White gel precipitate is immediately formed. It is allowed to settle for 12 h. Then it is filtered and washed with water 2–3 times. 0.27 g carbon black powder is mixed with filtered precipitate. The obtained mixture is dried for 24 h at 70ºC. Dried powder is crushed and heated at 600ºC for 4 h. Same procedure was repeated for $x = 0.05$ and 0.1 using different amounts of $FeSO_4 \cdot 7H_2O$ and $SnCl_2 \cdot 2H_2O$.

2.2 Method

The powder X-ray Diffraction (XRD) is recorded using Philips Holland, XRD system PW 1710 with nickel filtered CuKα ($\lambda = 1.5405$ Å) radiation. The average crystallite size (t) has been calculated from the line broadening using Scherrer's relation: $t = 0.9\lambda/B\cos\theta$, where λ is the wavelength of x-ray and B is the half maximum line width. Photoluminescence (PL) measurements are performed by F-4500 FL spectrophotometer with 150 W xenon lamp at room temperature. Powder samples are spread over a glass slide and mounted inside the sample holder. The transmission electron microscopy (TEM) is performed with Tecnai 20 G^2 under 200 KV. Samples are prepared by dispersing drop of colloid on copper grid, covered with the carbon film, and the solvent is evaporated. To record Fourier transform infra-red (FTIR) spectra, Bomem Hartmann & Braun MB Series Infrared spectrometer is used. SnO_2 powder is crushed with KBr particles (1 : 5) and pressed into thin pellets.

3 Results and discussion

3.1 XRD study

XRD patterns of $Sn_{1-x}Fe_xO_2$ ($x = 0, 0.02, 0.05, 0.1$) nanoparticles prepared at 600°C are shown in Figure 1. All the peaks of XRD belong to tetragonal lattice of SnO_2. The lattice parameters are calculated by using programme Unit Cell – method of TJB Holland & SAT Redfern 1995. The calculated lattice parameters of pure SnO_2 ($x = 0$) are $a = 4.723(1)$ Å, $c = 3.238(1)$ Å and its unit cell volume is $V = 72.24$ Å^3 and these values are well agreement with the reported values (JCPDS file No. 71-0652). The peaks are broad due to the nano-size effect. No trace of secondary phase is found. The unit cell volume increases slightly with Fe^{2+} doping indicating substitution of Sn^{4+} sites by Fe^{2+} ions. The unit cell volume increases from 72.24 Å^3 to 72.90 Å^3 as x varies from 0 to 0.1. With increases of Fe^{2+} concentration, the peaks in x-ray diffraction pattern are becoming broad because of strain effect from substitution of lower ionic radius of Sn^{4+} (0.69 Å) by large one Fe^{2+} (0.77 Å) [16]. The lattice parameters for $Sn_{1-x}Fe_xO_2$ ($x = 0, 0.02, 0.05, 0.1$) are given in Table 1. The crystallite size decreases from 21 nm to 11 nm when x varies from $x = 0$ to 0.1.

Figure 1 XRD patterns of pure SnO_2 and Fe^{2+} doped SnO_2 nanoparticles

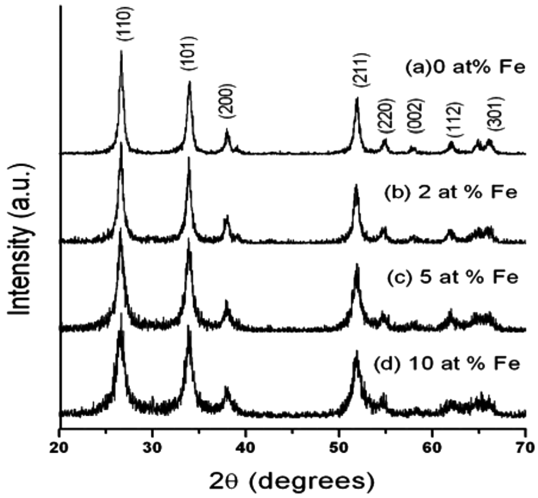
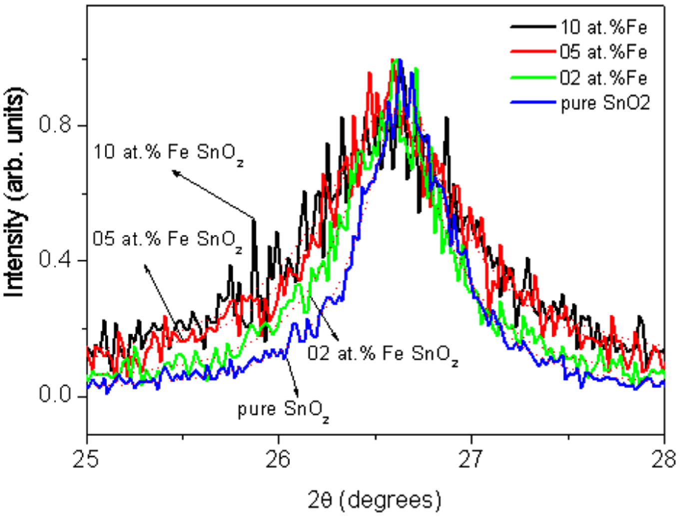


Table 1 Lattice parameters (a, c), unit cell volume (V) and crystallite size of $Sn_{1-x}Fe_xO_2$ ($x = 0, 0.02, 0.05, 0.1$)

x	a (Å)	c (Å)	V (Å^3)	*Crystallite size* (nm)
0.00	4.723(1)	3.238(1)	72.24	21
0.02	4.720(1)	3.250(1)	72.40	17
0.05	4.731(1)	3.240(1)	72.55	13
0.10	4.747(1)	3.234(1)	72.90	11

Figure 2 shows the XRD patterns of the strongest peak (110) for $Sn_{1-x}Fe_xO_2$ ($x = 0$, 0.02, 0.05, 0.1) nanoparticles. Each data are fitted with Lorentzian equation. The peak maxima are at $2\theta = 26.652$, 26.585, 26.582 and 26.572° for $x = 0$, 0.02, 0.05 and 0.1 respectively. It indicates the expansion of unit cell volume with Fe^{2+} doping in SnO_2. This is contrary to the reported values in Fe doped SnO_2, where unit cell volume decreases with Fe^{2+} doping in SnO_2 [17]. Fe^{2+} ions have two possible ionic sizes: 0.61 Å in case of low spin states and 0.77 Å in case of high spin states [16]. If Fe^{2+} ions with lower ionic size occupy Sn^{4+} (0.69 Å), the broadening of peaks will not occur in XRD patterns. In this study, the broadening occurs in XRD peaks indicating occupancy of Sn^{4+} ions by Fe^{2+} ions with higher ionic size. This is due to strain developed from substitution of lower ionic size by higher ionic size. In literature, it was reported that when La is substituted into V site of VN, broadening occurs since ionic size of La is more ionic size than that of V [18–20], whereas, if B substitutes N in VN, broadening does not occur since B and N have similar ionic radii [16,18–20]. Similarly, when Eu^{3+} ions occupy Y^{3+} sites of Y_2O_3, broadening does not occur since both have similar ionic sizes [21]. In addition to this, Fe^{2+} has 2+ charge and Sn^{4+} has 4+ charge, i.e., charge imbalance occurs when substitution takes place in SnO_2 system. This may give rise to vacancy in oxygen lattice.

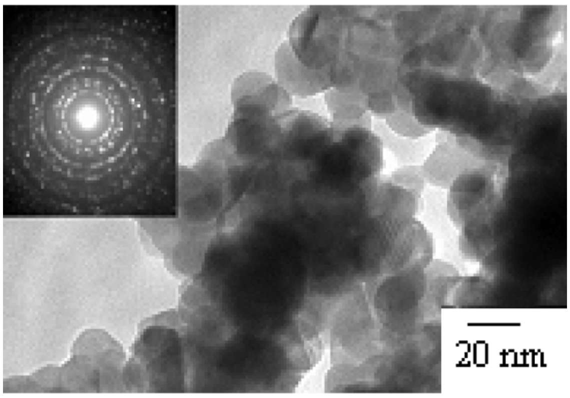
Figure 2 XRD patterns of the strongest peak (110) for pure SnO_2 and Fe^{2+} doped SnO_2 nanoparticles. Dots indicate the fit to data using Lorentzian equation (see online version for colours)



3.2 *TEM study*

Figure 3 shows TEM micrograph of pure SnO_2 nanoparticles prepared at 600°C. The average grain size obtained from TEM microstructure is nearly 25 nm. It is slightly more than crystallite size obtained from XRD analysis (21 nm) using Scherrer's formula. Inset of Figure 3 shows its Selected Area Electron Diffraction (SAED) pattern. From this tetragonal patterns of spots are observed indicating the high crystallinity of particles.

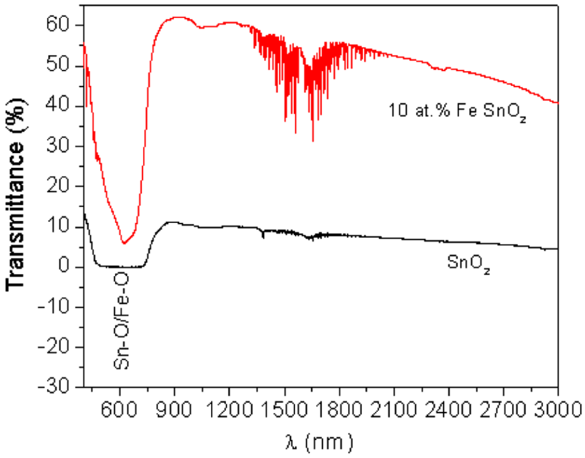
Figure 3 TEM image of pure SnO_2 particles and inset shows its SAED patterns



3.3 *FTIR study*

FTIR spectra of pure SnO_2 and 10 at. % Fe doped SnO_2 ($x = 0.1$) nanoparticles prepared at 600°C are shown in Figure 4. The broad peak centred at 650 cm^{-1} is observed. The broad band between 800 cm^{-1} and 500 cm^{-1} was due to the vibrations of Sn-O/Fe-O bond [18–20,21].

Figure 4 IR spectra of pure SnO_2 and 10 at. % Fe^{2+} doped SnO_2 nanoparticles (see online version for colours)



3.4 *Luminescence study*

The room temperature photoluminescence spectra of pure SnO_2 and Fe^{2+} doped SnO_2 nanoparticles prepared at 600ºC after excitation at 250 nm are shown in Figure 5. Three main peaks are observed at 400, 471 and 545 nm. The peak at 400 nm is due to band edge emission [22,23]. The sharp peak at 471 nm arises due to artifact [22]. The broad peak at 545 nm is due to oxygen deficiency or surface trap emission [24]. Interestingly, emission intensity decreases with Fe^{2+} doping in SnO_2 indicating that Fe^{2+} ions are quenching centres/killers in luminescence. Figure 6 shows the excitation spectra of pure SnO_2 and Fe^{2+} doped SnO_2 nanoparticles monitored at 545 nm emission. Band-edge absorption is obtained around 300–350 nm for all samples. Such value is similar to the reported ones [22,23].

Figure 5 Luminescence spectra of pure SnO_2 and Fe^{2+} doped SnO_2 nanoparticles (see online version for colours)

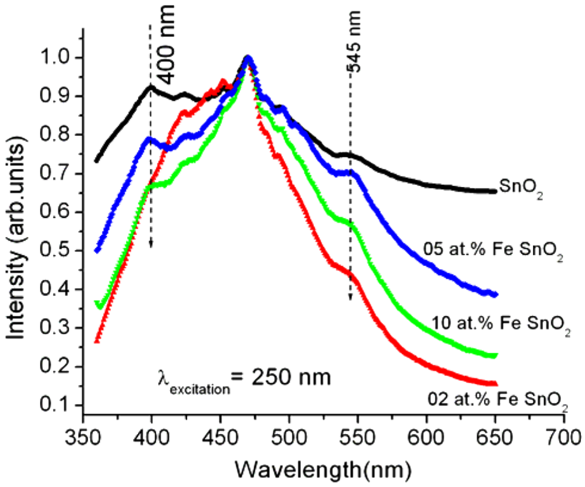
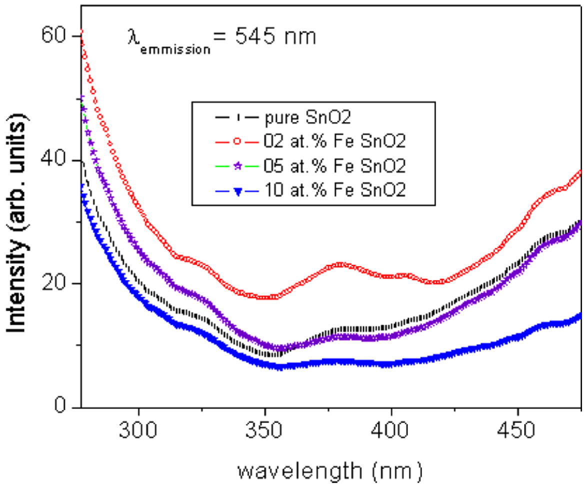


Figure 6 Excitation spectra of pure SnO_2 and Fe^{2+} doped SnO_2 nanoparticles (see online version for colours)



4 Conclusions

Fe^{2+} ions are doped into SnO_2 lattice successfully. Unit cell volume increases with Fe^{2+} ions incorporation in SnO_2. Luminescence intensity decreases with Fe^{2+} doping indicating that Fe^{2+} ions act as quenching centres or killers. Band edge emission is obtained at ~400 nm for all samples.

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References

1 Ningthoujam, R.S. and Kulshreshtha, S.K. (2009) 'Nanocrystalline SnO_2 from thermal decomposition of tin citrate crystal: luminescence and Raman studies', *Mater. Res. Bull.*, Vol. 44, pp.57.

2 Khandelwal, R., Singh, A.P., Kapoor, A., Grigorescu, S., Miglietta, P., Stankova, N.E. and Perrone, A. (2009) 'Effects of deposition temperature on the structural and morphological properties of SnO_2 films fabricated by pulsed laser deposition', *Opt. Laser Technol.*, Vol. 41, pp.89.

3 Vasu, V. and Subramanyan, A. (1990) 'Electrical and optical properties of sprayed SnO_2 films: Dependence on the oxidising agent in the starting material', *Thin Solid Films*, Vols. 193–194, pp.973.

4 Ni, J., Zhao, X., Zheng, X., Zhao, J. and Liu, B. (2009) 'Electrical, structural, photoluminescence and optical properties of p-type conducting, antimony-doped SnO_2 thin films', *Acta Mater.*, Vol. 57, pp.278.

5 Kilic, C. and Zunger, A. (2002) 'Origins of coexistence of conductivity and transparency in SnO_2', *Phys. Rev. Lett.*, Vol. 88, p.095501.

6 Lee, Y.I.., Lee, K.J., Lee, D.H., Jeong, Y.K., Lee, H.S. and Choa, Y.H. (2009) 'Preparation and gas sensitivity of SnO_2 nanopowder homogenously doped with Pt nanoparticles', *Curr. Appl Phys.*, Vol. 9, pp.S79.

7 Bouzidi, C., Elhouichet, H., Moadhen, A. and Oueslati, M. (2009) 'Sensitisation of erbium emission by silicon nanocrystals-doped SnO_2', *J. Lumin.*, Vol. 129, p.30.

8 Rella, R., Serra, A. and Siciliano, P. (1997) 'Tin oxide-based gas sensors prepared by the sol–gel process', *Sens. Actuators, B*, Vol. 44, pp.462.

9 Ray, S.C., Karanjai, M.K. and Dasgupta, D. (1997) 'Preparation and study of doped and undoped tin dioxide films by the open air chemical vapor deposition technique', *Thin Solid Films*, Vol. 307, pp.221.

10 Shishkin, N.Y., Zharsky, I.M. and Lugin, V.G. (1998) 'Air sensitive tin dioxide thin films by magnetron sputtering and thermal oxidation technique', *Sens. Actuators, B*, Vol. 48, pp.403.

11 Baik, N.S., Sakai, G. and Miura, N. (2000) 'Hydrothermally treated sol solution of tin oxide for thin-film gas sensor', *Sens. Actuators, B*, Vol. 63, pp.74.

12 Gu, F., Wang, S.F., Lu, M.K., Zhou, G.J., Xu, D. and Yuan, D.R. (2004) 'Photoluminescence properties of SnO_2 nanoparticles synthesized by sol−gel method', *J. Phys. Chem. B*, Vol. 108, pp.8119.

13 Janisch, R., Gopal, P. and Spaldin, N. (2005) 'Transition metal-doped TiO_2 and ZnO- present status of the field', *J. Phys.: Condens. Matter.*, Vol. 17, pp.R657.

14 Liu, C.M., Zu, X.T. and Zhou, W.L. (2006) 'Magnetic interaction in Co-doped SnO_2 nano-crystal powders', *J. Phys.: Condens. Matter.*, Vol. 18, pp.6001.

15 Punnoose, A., Hays, J., Thuber, A., Engelhard, M.H., Kukkadapu, R.K., Wang, C., Shutthanandan, V. and Thevuthasan, S. (2005) 'Development of high-temperature ferromagnetism in SnO_2 and paramagnetism in SnO by Fe doping', *Phys. Rev. B: Condens. Matter*, Vol. 72, pp.054402.

16 Shannon, R.D. and Prewitt, C.T. (1969) 'Effective ionic radii in oxides and fluorides', *Acta Cryst*., Vol. B25, pp.925.

17 Hays, J., Thurber, A., Reddy, K.M. and Punnoose, A. (2007) 'Magnetism in Fe- and Co-doped tin oxide nanoparticles', in Hong, N.H. (Ed.): *Transworld Research Network*, 37/661 (2), Fort P.O. Trivandrum, Kerala, India.

18 Ningthoujam, R.S., Sudhakar, N., Rajeev, K.P. and Gajbhiye, N.S. (2002) 'Electrical resistivity study of La, B doped nanocrystalline superconducting vanadium nitride', *J. Appl. Phys.*, Vol. 91, pp.6051.

19 Ningthoujam, R.S. and Gajbhiye, N.S. (2004) 'Magnetic and current density studies on nanostructured vanadium nitride material', *Indian J. Phys.*, Vol. 78, No. A(1), pp.89.

20 Sudhakar, N., Ningthgoujam, R.S., Rajeev, K.P., Nigam, A.K., Weissmuller, J. and Gajbhiye, N.S. (2004) 'Effect of La, B doping on the electrical resistivity and magnetic susceptibility of nanocrystalline vanadium nitride', *J. Appl. Phys.*, Vol. 96*,* p.688.

21 Singh, L.R., Ningthoujam, R.S., Sudarsan, V., Srivastava, I., Dorendrajit Singh, S., Dey, G.K. and Kulshreshtha, S.K. (2008) 'Luminescence study on Eu^{3+} doped Y_2O_3 nanoparticles: particle size, concentration and core–shell formation effects', *Nanotechnology*, Vol. 19, pp.055201.

22 Ningthoujam, R.S., Sudarsan, V. and Kulshreshtha, S.K. (2007) 'SnO_2: Eu nanoparticles dispersed in silica: a low-temperature synthesis and photoluminescence study', *J. Lumin.*, Vol. 127, pp.747.

23 Ningthoujam, R.S., Debdutta, L., Sudarsan, V., Poswal, H.K., Kulshreshtha, S.K., Sharma, S.M., Bhushan, B. and Sastry, M.D. (2007) 'Nature of V^{n+} ions in SnO_2: EPR and photoluminescence studies', *Mater. Res. Bull.*, Vol. 42, pp.1293.

24 Maestre, D., Cremades, A. and Piqueras, J. (2005) 'Growth and luminescence properties of micro- and nanotubes in sintered tin oxide', *J. Appl. Phys.*, Vol. 97, pp.044316.