



# Synthesis, characterization, and FTIR study on $\text{Sn}_{1-x}\text{Mn}_x\text{O}_2$ powders

A.A. Dakhel

Department of Physics, College of Science, University of Bahrain, P.O. Box 32038, Kingdom of Bahrain

## ARTICLE INFO

### Article history:

Received 8 May 2012

Received in revised form 5 December 2012

Accepted 7 December 2012

Available online 22 December 2012

### Keywords:

$\text{Sn}_{1-x}\text{Mn}_x\text{O}_2$  powder

Mn-doped  $\text{SnO}_2$  powder

Oxygen vacancies

Blue shift

## ABSTRACT

A mixture of  $\text{SnCl}_2$  and tris(acetylacetonato)manganese(III) complex was thermally co-decomposed to synthesize Mn-doped  $\text{SnO}_2$  powders. Two preparation routes were conducted: in the first route, the samples were annealed in air and in the second route, the samples were further annealed in high vacuum. The elemental and crystalline structures of the prepared powders were studied by the X-ray fluorescence (XRF) and X-ray diffraction (XRD) methods. It was confirmed that all the incorporated Mn ions doped in  $\text{SnO}_2$  forming  $\text{Sn}_{1-x}\text{Mn}_x\text{O}_2$  substitutional solid solution ( $x=0.000, 0.014, 0.024, 0.068$ ). The samples were subjected to an extensive optical characterisation with FTIR and optical absorption methods. The doping processes as well as the vacuum-annealing effect were studied by FTIR method. The optical absorption spectroscopy was used to observe the dependence of the absorption onset on the Mn-doping level. Annealing in vacuum was proved to create more oxygen vacancies.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Tin oxide ( $\text{SnO}_2$ ) has high optical transparency, wide bandgap (~3.6 eV), and degenerate semiconducting electrical properties [1]. Therefore,  $\text{SnO}_2$  has many different applications in field of optoelectronic devices [2,3], transparent conducting oxides (TCO) [4,5], gas sensing [6–8], etc. The effect of doping of  $\text{SnO}_2$  with different metallic ions was investigated for application in various purposes [9]. For example, it was doped with a few percent of 3d transition-metal (TM) ions in order to fabricate diluted magnetic semiconductors (DMS) of Curie temperature around room temperature (RT-FM) [10–15]. Thus, Mn-doped  $\text{SnO}_2$  solid solution was investigated for FM applications. Different models were proposed to explain the interactions responsible for the appearance of FM behavior in such materials. One of them [16] attributes the appearance of FM to the exchange interaction between the TM ions substituting tin ions in host  $\text{SnO}_2$  lattice that involve an electron trapped at an oxygen vacancy (F-center exchange). Another model is called the bound magnetic polaron (BMP) model [14]. Generally, it was confirmed that the appearance of FM is very sensitive to the procedure of sample preparation method and thus the crystalline structure and concentration of oxygen vacancies and defects [17]. Therefore, it is not surprising to observe no FM in the Mn-doped  $\text{SnO}_2$  samples sintered at high temperature (800 °C), irrespective of the doping content, while the samples sintered at low temperature (450 °C) possess FM when the doping content was below 5% [18]. These results were explained by BMP model. Choudhury et al. [19] have studied Co-doped  $\text{TiO}_2$  samples and found that the samples annealed in an open air were

paramagnetic and those annealed in vacuum exhibited RT-FM. Thus, the created oxygen vacancies due to the annealing in vacuum are responsible for the observed RT-FM and their results were explained by BMP model. Therefore, it is important to have an experimental evidence for the creation of oxygen vacancies in vacuum annealing of Mn-doped  $\text{SnO}_2$ . This is one of the goals of the present work.

In the present fundamental work,  $\text{Sn}_{1-x}\text{Mn}_x\text{O}_2$  powders with  $x=0.000, 0.014, 0.024, 0.068$  were synthesized by chemical co-precipitation method. The annealing of the powders was done by two routes, first in air and second in vacuum in order to create oxygen vacancies. The current investigation focuses on the effects of Mn doping on the optical (UV–VIS and FTIR) and structural properties of the host  $\text{SnO}_2$ , especially such studies are still few.

## 2. Experimental procedure

Mn-doped  $\text{SnO}_2$  powders with different Mn compositions were synthesized by simple chemical coprecipitation route. Appropriate by weight amounts of pure  $\text{SnCl}_2$  and tris(acetylacetonato)manganese(III) [ $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ] were totally dissolved in acetone in one ceramic pot with constant stirring at room temperature getting a solution. The solution was left at room temperature for 24 h until total natural drying in order to get the gel. Finally, the gel was sintered in a closed furnace at temperatures 600 °C for 1 h in air followed by natural cooling in the furnace to room temperature. These precursors were good grounded and pelletized under 750 MPa pressure. Some of these pellets were further annealed in vacuum of about  $10^{-5}$  Torr at 500 °C for 20 min.

The elemental analyses of the samples were made with energy dispersive X-ray fluorescence (EDX) spectroscopy method. The setup used consists of a Philips PW-1710 X-ray tube with a Cu

E-mail address: [adakhil@sci.uob.bh](mailto:adakhil@sci.uob.bh).

anode operated at 15 kV, 5 mA and a sensitive Amptek XR-100CR detector. The Mn molar content in the examined samples ( $x$ ) was 0% (undoped), 1.4, 2.4 and 6.8%. The sample was named according to its  $x$ . The sample structures were studied with by a Philips PW-1710  $\theta$ - $2\theta$  X-ray diffraction (XRD) equipped with Cu anode (0.15406 nm) and a step size of  $0.02^\circ$ . Fourier-transform infrared (FTIR) spectra were measured at room temperature on an IR Prestige-21/Shimadzu Spectrometer using the KBr disk technique. The measurements were conducted in an absorbance mode within the frequency range of  $4000$ – $200\text{ cm}^{-1}$ . The UV–VIS absorption spectra were recorded on a Shimadzu UV-3600 scanning spectrophotometer using a 1 cm path-length quartz cell. The UV–VIS spectrum was obtained for the well-milled powder sample, which had been ultra-sonicated in a double deionised water to yield homogeneous dispersions. Pure deionised water was used as a blank.

### 3. Results and discussion

#### 3.1. Characterisation by X-rays

Fig. 1 shows the EDX spectrum of the prepared samples. Each spectrum shows Mn  $K_{\alpha}$  (5.898 keV) band, Sn  $L_{\alpha}$  (3.444 keV), Sn  $L_{\beta 1}$  (3.662 keV) band, and signal from the Cu source of the X-ray tube. No other signals were detected. The relative fraction ratios of Mn to Sn in the samples were determined by measuring the ratio of the integral intensity of Mn  $K_{\alpha}$ -signal to that of Sn  $L_{\alpha, \beta 1}$ -band and using the known method of micro radiographic analysis [20]. The reference samples were pure SnCl<sub>2</sub> and tris(acetylacetonato)manganese(III).

Fig. 2 shows the XRD patterns of the prepared samples annealed in air (Fig. 2a) and in vacuum (Fig. 2b). For comparison, the XRD pattern of the undoped SnO<sub>2</sub> powder prepared by the same preparation procedure is also shown on the same figure. The peaks of the polycrystalline samples were indexed according to the known rutile tetragonal phase (space group  $P4_2/mnm$ ) of SnO<sub>2</sub> [21]. The orthorhombic phase of SnO<sub>2</sub>, SnO and other forms of tin oxide were not detected in the present samples. Diffraction reflections arising from Mn, Mn oxides or any Mn related phases were not detected. The most expected secondary phase Mn<sub>2</sub>O<sub>3</sub> Oxide, which usually crystallizes by annealing at  $500^\circ\text{C}$  was also not detected. This means that all the added manganese ions were doped in the SnO<sub>2</sub> crystalline structure. It should be mentioned here that it was found that Mn ions are soluble into SnO<sub>2</sub> up to 30 mol% [22] or 11 mol% [14]. Table 1 shows the lattice parameters of the prepared pure and Mn-doped

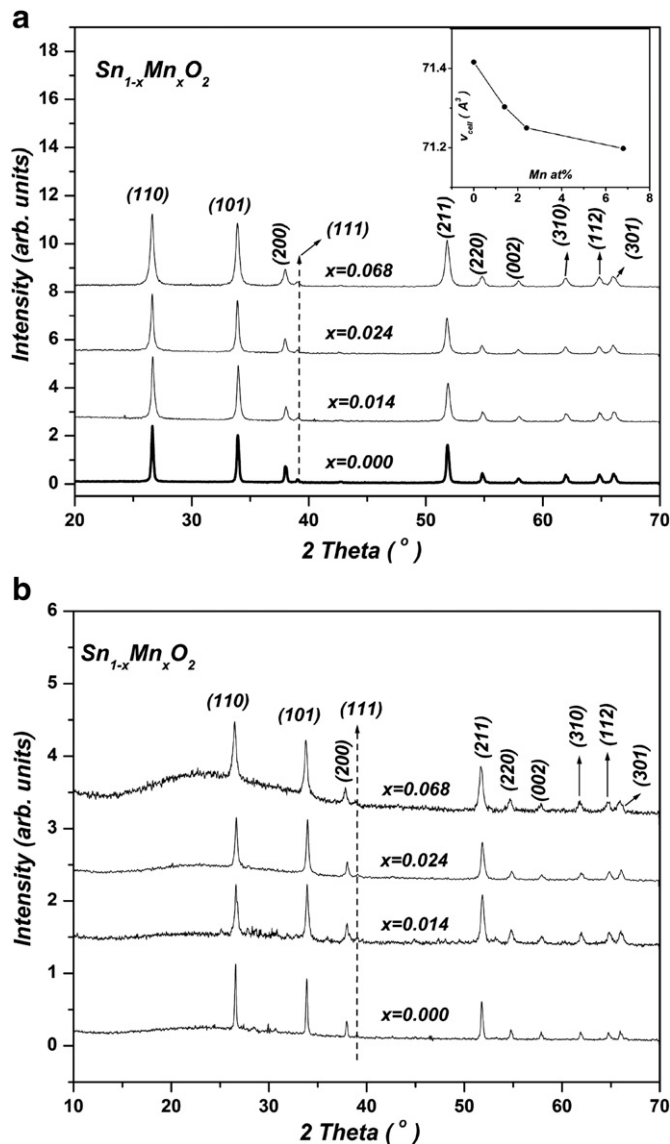


Fig. 2. X-ray diffraction patterns of pure and Mn-doped SnO<sub>2</sub> powder samples at different doping levels annealed in air (a) and in vacuum (b).

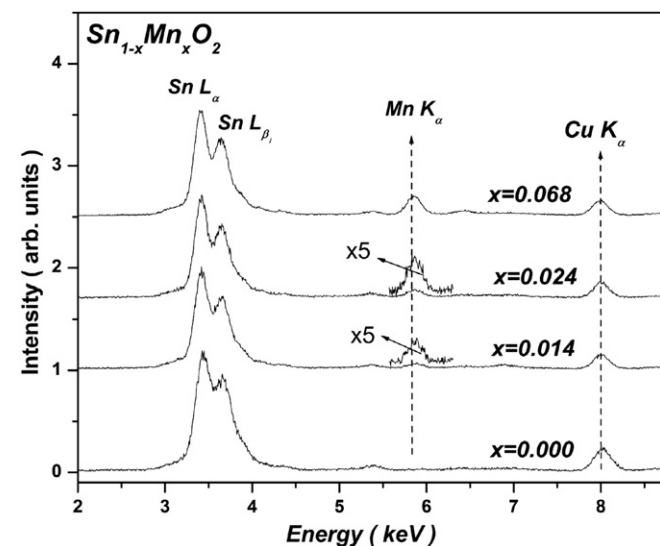


Fig. 1. Energy-dispersive X-ray fluorescence spectra of pure and Mn-doped SnO<sub>2</sub> pressed powder disk. The Mn  $K_{\alpha}$  band enlarged five times.

SnO<sub>2</sub> powders. These parameters were calculated by using the known computer program “Unitcell”. The obtained lattice parameters are close to the standard ones:  $a = b = 4.738\text{ \AA}$  and  $c = 3.188\text{ \AA}$  [21]. The volume of the unit cell ( $V_{\text{cell}}$ ), as shown in the inset of Fig. 2a, is slightly reduced with Mn doping that agrees with the other published works [18,23,24]. The present-work annealing in vacuum has undetectable effect on the lattice parameters. However, the reduction in the unit-cell volume with Mn doping is expected since the doped Mn<sup>3+</sup> ions have slightly smaller size than that of hosts Sn<sup>4+</sup> ions [14]. The Shannon radius of 6-coordination Sn<sup>4+</sup> ion is 0.069 nm while that of Mn<sup>3+</sup> is 0.0645 [25]. From the defect point of view,

Table 1

SnO<sub>2</sub> structure lattice parameters ( $a$ ,  $c$ , and volume of unit cell  $V_{\text{cell}}$ ), micro-strain ( $\epsilon_s$ ), structural stress ( $\sigma_{\text{st}}$ ), and bandgap of the prepared undoped and Mn-doped SnO<sub>2</sub> powders.

Sample	$a$ (Ang)	$c$ (Ang)	$V_{\text{cell}}$ (Ang <sup>3</sup> )	$\epsilon_s$ ( $10^{-3}$ )	$\sigma_{\text{st}}$ (GPa)	$E_g$ (eV)
SnO <sub>2</sub> ( $x=0$ )	4.736	3.184	71.416	Ref	Ref	3.5
$x=1.4\%$	4.733	3.183	71.303	1.58	323.9	3.6
$x=2.4\%$	4.732	3.182	71.25	2.32	475.6	4.3
$x=6.8\%$	4.731	3.181	71.198	3.05	625.3	4.5

Download English Version:

<https://daneshyari.com/en/article/236850>

Download Persian Version:

<https://daneshyari.com/article/236850>

[Daneshyari.com](https://daneshyari.com)