Studying Structural Properties and Fourier Transformation Infrared Spectrum of Sb Doped SnO₂ Powders Prepared by Solid State Reaction

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Abstract

Sb doped tin oxide transparent conducting powder were prepared by solid state reaction method. Structural properties of the samples were investigated as a function of various Sb-doping levels (x=0.00-0.01-0.02-0.04-0.06). The results of x-ray diffraction have shown that the samples are polycrystalline structure in tetragonal phase with preferential orientations along the (110) and (101) planes. The relative intensities, distance between crystalline planes (d), crystallite size (D), dislocation density (d) and lattice parameters (a), (c) were determined. Infrared Spectroscopy have been studied by Infrared Spectrometer Device.

Keywords: powder, Antimony doped Tin Oxide, solid state reaction, Structural properties, Infrared Spectroscopy.

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1. Introduction

Nano-crystals of semiconductor metal oxides have attracted a great interest due to their intriguing properties, which are different from those of their corresponding bulk state [1]. Tin dioxide SnO₂ has achieved special attention among the metal oxides, because of its wide band gap (3.6eV), optical transparency and high carrier density, thermal and chemical stabilities [2, 3].

Because of its unique electronic, optical, electrochemical and catalytical properties, it has been widely used in flat panel displays, transparent conducting electrodes, solar cells, gas sensors and rechargeable Li – ion batteries, etc [4].

It crystallizes in the tetragonal rutile structure with space group P42/mnm. the lattice parameters a = b = 4.738 Å and c = 3.187 Å [5].

Its unit cell contains two tin and four oxygen atoms as is shown in figure (1). The tin atom is at the center of six oxygen atoms placed at the corners of a regular octahedron. Every oxygen atom is surrounded by three tin atoms at the corners of an equilateral triangle [6].

Fig (1) : Unit cell of the crystal structure of SnO₂. Large circles indicate oxygen atoms and the small circles indicate tin atoms.

The aim of this paper is preparing a doped metal oxide Sn₁₋ₓSbₓO₂ and characterizing by X-ray and FTIR to study the structural properties.

2. Experimental Method

Sn₁₋ₓSbₓO₂ powders (x = 0.00 - 0.01 - 0.02 - 0.04 - 0.06) were prepared by a solid state reaction method. were accurately weighed in required proportions and were mixed and ground thoroughly using an Agate mortar and pestle to convert to very fine powders.

The grinding of the mixtures was carried out for 3 hours for all the powder samples. The ground powder
samples were firing at 700°C for 3 hours.

3. Results and discussions

3.1 Structural properties

The X-ray diffraction patterns of undoped and Sb doped SnO₂ powders prepared with various Sb concentration 0 wt%, 1 wt%, 2 wt%, 4 wt% and 6 wt% are shown in Figure (2). The XRD reveals that all samples are having polycrystalline nature with tetragonal structure and peaks correspond to (110), (101), (200), (111), (210), (211), (220), (002), (310), (112), (301), (202) and (321) planes. The preferred orientation is (110) for pure and Sb doped SnO₂ powders at 1 and 4 wt% doping, but for 2 and 6 wt% doping the preferred orientation change to (101) plane.

Fig (2): XRD results of pure SnO₂, 1 wt% Sb doped SnO₂, 2 wt% S doped SnO₂, 4 wt% Sb doped SnO₂, 6 wt% Sb doped SnO₂.
Table (1) shows results of structural values of undoped SnO$_2$ sample.

| samples       | 2θ (deg) | hkl | d (Å) | Rel. int. [%] | β (deg) | D (nm) | Average D (nm) | δ $10^{15}$ line/m$^2$ | Lattice const. |
|---------------|----------|-----|-------|--------------|---------|--------|---------------|----------------------|---------------|
| SnO$_2$ pure  | 26.62    | (110) | 3.348 | 100          | 1.392   | 6.128  |               |                      |               |
|               | 33.99    | (101) | 2.637 | 87           | 1.391   | 6.240  |               |                      |               |
|               | 37.95    | (200) | 2.370 | 25           | 0.886   | 9.908  |               |                      |               |
|               | 38.96    | (111) | 2.311 | 7            | 0.440   | 20.012 |               |                      |               |
|               | 42.62    | (210) | 2.121 | 4            | 0.510   | 17.471 |               |                      |               |
|               | 51.87    | (211) | 1.762 | 58           | 1.265   | 7.297  |               |                      |               |
|               | 54.75    | (220) | 1.676 | 58           | 0.506   | 18.473 |               |                      |               |
|               | 57.87    | (002) | 1.593 | 11           | 1.012   | 9.372  |               |                      |               |
|               | 61.99    | (310) | 1.497 | 14           | 1.341   | 7.221  |               |                      |               |
|               | 64.84    | (112) | 1.437 | 17           | 1.898   | 5.180  |               |                      |               |
|               | 65.96    | (301) | 1.416 | 15           | 0.632   | 15.656 |               |                      |               |
|               | 71.25    | (202) | 1.323 | 7            | 1.645   | 6.207  |               |                      |               |
|               | 78.30    | (321) | 1.221 | 10           | 0.424   | 25.240 |               |                      |               |

Table (2) shows results of structural values of Sb doped SnO$_2$ samples (x=0.01-0.02).

| samples       | 2θ (deg) | hkl | d (Å) | Rel. int. [%] | β (deg) | D (nm) | Average D (nm) | δ $10^{15}$ line/m$^2$ | Lattice const. |
|---------------|----------|-----|-------|--------------|---------|--------|---------------|----------------------|---------------|
| SnO$_2$:Sb (1 wt%) | 26.62    | (110) | 3.345 | 100          | 1.15    | 7.414  |               |                      |               |
|               | 33.89    | (101) | 2.642 | 72           | 1.45    | 5.982  |               |                      |               |
|               | 38.15    | (111) | 2.357 | 15           | 2.01    | 4.367  |               |                      |               |
|               | 42.51    | (210) | 2.124 | 4            | 0.82    | 10.857 |               |                      |               |
|               | 51.98    | (211) | 1.757 | 55           | 1.49    | 6.195  |               |                      |               |
|               | 58.32    | (002) | 1.580 | 8            | 1.85    | 5.135  |               |                      |               |
|               | 62.23    | (310) | 1.490 | 11           | 1.79    | 5.414  |               |                      |               |
|               | 65.36    | (301) | 1.426 | 13           | 2.42    | 4.073  |               |                      |               |
|               | 71.86    | (202) | 1.312 | 6            | 1.95    | 5.254  |               |                      |               |
|               | 78.25    | (321) | 1.220 | 10           | 2.13    | 5.021  |               |                      |               |

Table (2) shows results of structural values of Sb doped SnO$_2$ samples (x=0.01-0.02).

| samples       | 2θ (deg) | hkl | d (Å) | Rel. int. [%] | β (deg) | D (nm) | Average D (nm) | δ $10^{15}$ line/m$^2$ | Lattice const. |
|---------------|----------|-----|-------|--------------|---------|--------|---------------|----------------------|---------------|
| SnO$_2$:Sb (2 wt%) | 26.85    | (110) | 3.317 | 80           | 1.85    | 4.611  |               |                      |               |
|               | 33.94    | (101) | 2.639 | 100          | 1.15    | 7.543  |               |                      |               |
|               | 37.96    | (200) | 2.368 | 12           | 1.56    | 5.624  |               |                      |               |
|               | 43.25    | (210) | 2.090 | 6            | 2.12    | 4.210  |               |                      |               |
|               | 52.16    | (211) | 1.752 | 68           | 1.25    | 7.390  |               |                      |               |
|               | 58.2     | (002) | 1.583 | 9            | 1.46    | 6.504  |               |                      |               |
|               | 61.95    | (310) | 1.496 | 7            | 1.77    | 5.467  |               |                      |               |
|               | 65.78    | (301) | 1.418 | 13           | 1.95    | 5.067  |               |                      |               |
|               | 71.35    | (202) | 1.320 | 4            | 2.22    | 4.600  |               |                      |               |
|               | 78.99    | (321) | 1.211 | 9            | 1.68    | 6.400  |               |                      |               |
Table (3) shows results of structural values of Sb doped SnO\textsubscript{2} samples (x=0.04-0.06).

| samples          | 2θ (deg) | hkl  | d (Å) | Rel. int. [%] | β (deg) | D (nm) | Average D (nm) | δ 10\(^{18}\) line/m\(^2\) | Lattice const. |
|------------------|----------|------|-------|--------------|---------|--------|--------------|-----------------|----------------|
|                  |          |      |       |              |         |        |              |                              |                |
| SnO\textsubscript{2}:Sb (4 wt%) |          |      |       |              |         |        |              |                              |                |
|                  | 26.63    | (110)| 3.344 | 100          | 1.92    | 4.440  | 6.532        | 50.705          | 4.730 3.129     |
|                  | 34.12    | (101)| 2.625 | 80           | 1.83    | 4.742  |              | 44.456          |                  |
|                  | 38.1     | (111)| 2.360 | 10           | 1.52    | 5.775  |              | 29.983          |                  |
|                  | 42.22    | (210)| 2.138 | 5            | 1.35    | 6.588  |              | 23.038          |                  |
|                  | 52.27    | (211)| 1.748 | 69           | 1.75    | 5.281  |              | 35.852          |                  |
|                  | 58.98    | (002)| 1.564 | 7            | 0.98    | 9.726  |              | 10.569          |                  |
|                  | 61.85    | (310)| 1.498 | 9            | 1.15    | 8.410  |              | 14.136          |                  |
|                  | 65.34    | (301)| 1.427 | 15           | 2.1     | 4.693  |              | 45.390          |                  |
|                  | 71.52    | (202)| 1.318 | 4            | 1.12    | 9.129  |              | 11.997          |                  |
| SnO\textsubscript{2}:Sb (6 wt%) |          |      |       |              |         |        |              |                              |                |
|                  | 26.25    | (110)| 3.392 | 94           | 1.52    | 5.605  | 5.186        | 31.828          | 4.797 3.150     |
|                  | 33.88    | (101)| 2.643 | 100          | 1.75    | 4.956  |              | 40.706          |                  |
|                  | 38.02    | (111)| 2.364 | 15           | 1.86    | 4.718  |              | 44.919          |                  |
|                  | 52.21    | (211)| 1.750 | 48           | 1.96    | 4.714  |              | 44.995          |                  |
|                  | 58.56    | (002)| 1.575 | 7            | 1.62    | 5.872  |              | 29.001          |                  |
|                  | 61.84    | (310)| 1.499 | 4            | 2.15    | 4.498  |              | 49.414          |                  |
|                  | 65.15    | (301)| 1.430 | 16           | 1.65    | 5.967  |              | 28.081          |                  |
|                  | 70.85    | (202)| 1.328 | 6            | 1.82    | 5.594  |              | 31.948          |                  |
|                  | 78.15    | (321)| 1.222 | 10           | 2.25    | 4.750  |              | 44.316          |                  |

The relative intensities of undoped and Sb doped SnO\textsubscript{2} powders are calculated. The distance between crystalline planes values (d) are calculated by using following relation:

\[ 2d \sin \theta = n \lambda \] (1)

Where \( d \) is distance between crystalline planes (Å), \( \theta \) is the Bragg angle, \( \lambda \) is the wavelength of X-rays (\( \lambda = 1.54056 \) Å).

The crystallite size is calculated from Scherrer’s equation [7]:

\[ D = \frac{0.0942}{\beta \cos \theta} \] (2)

Where, D is the crystallite size, \( \lambda \) is the wavelength of X-ray, \( \beta \) is full width at half maximum (FWHM) intensity in radians and \( \theta \) is Bragg’s angle.

The dislocation density is defined as the length of dislocation lines per unit volume and calculated by following equation [8]:

\[ \delta = \frac{1}{\beta \cos \theta} \] (3)

The lattice constants \( a \) and \( c \) for tetragonal phase structure are determined by the relation [9]:

\[ \frac{1}{\alpha^2} = \frac{n^2+k^2}{a^2} + \frac{l^2}{c^2} \] (4)

Where \( d \) and (hkl) are distance between crystalline planes and Miller indices, respectively.

The calculated lattice constants \( a, c \) values are given in table 1,2,3. It was seen that \( a, c \) and \( c/a \) match well with JCPDS data (\( a=b= 4.737 \) Å and \( c= 3.185 \) Å).

The change in peak intensities is basically due to the replacement of Sn\textsuperscript{4+} ions with Sb\textsuperscript{5+} ions in the lattice of the SnO\textsubscript{2}.

Figure (3) represents variation of the average grain size with different concentrations of Sb doped SnO\textsubscript{2} powders.
We observed that the crystallite size decreases with increasing of the antimony ion content. This is due to the fact that the Sb^{5+} (0.62 Å) radius is smaller than the Sn^{4+} (0.69 Å), and the replacement process which causes shrinkage of the lattice [10, 11].

4. FT/IR analysis:

![FTIR analysis of pure and Sb doped SnO₂ powder](image)

FTIR is a technique used to obtain information regarding chemical bonding and functional groups in a material. In the transmission mode, it is quite useful to predict the presence of certain functional groups which are adsorbed at certain frequencies; thus, it reveals the structure of the material. The band positions and numbers of absorption peaks depend on the crystalline structure, chemical composition, and also on morphology [12]. To investigate chemical groups on the surface of sintered samples, an FTIR analysis was carried out at room temperature over the wave number range of 400–4000 cm⁻¹. There are several bands appearing in the wave number range 400–4000 cm⁻¹. The broad absorption band at 3423 cm⁻¹, the peaks at 2977 cm⁻¹, and 1630 cm⁻¹ are assigned to the vibration of hydroxyl group due to the absorbed/adsorbed water and show a stretching vibrational mode of O–H group [13]. Absorption peaks observed around 2380 cm⁻¹ belong to the stretching vibrations of C–H bonds.
that could be due to the adsorption and interaction of atmospheric carbon dioxide with water during the firing process [14]. The main IR features of SnO$_2$ appear at 468 and 609 cm$^{-1}$, which assign to O–Sn–O and Sn–O stretching vibration, respectively [15]. The changing in the shapes and positions of absorption peaks indicates to presence of stretching modes, which are, give an indication of successful doping Sb to tin oxide nanoparticles [16].

5. Conclusion
This paper presents a study of structural properties of Sb doped SnO$_2$ powders prepared by solid state reaction method. X-ray diffraction patterns confirm that the samples have polycrystalline nature with tetragonal structure and show presence (110) (101) (111) (210) (211) (220) (002) (310) (301) (202) and (321) planes in pure tin oxide sample. The SnO$_2$ have preferred orientation along (110) for all samples, but for (0.02, 0.06) doping levels the preferred orientation change to (101) plane. The average of crystallite size is within the range [11.877- 5.186 nm] for all samples. It was defined that the lattice constants a, c for all the samples, were almost identical with JCPDS values, and the ratio c/a remained constant with increasing Sb dopant concentration. FTIR analysis revealed that the Sb doping manifests itself by a shift in Sn–O absorption peaks positions.

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