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Studying Effect of Fe Doping on the Structural Properties and Infrared Spectroscopy of Tin Oxide powders by Solid State Reaction Method

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Abstract
Fe 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 Fe-doping levels (x=0.00-0.01-0.03-0.05-0.06). The results of x-ray diffraction have shown that the samples are polycrystalline structure in tetragonal phase with preferential orientations along the (110) for all samples The relative intensities, distance between crystalline planes (d), crystallite size (D), dislocation density (δ) and lattice parameters (a), (c) were determined. Infrared Spectroscopy have been studied by Infrared Spectrometer Device.
Keywords: powder, Iron doped Tin Oxide, solid state reaction, Structural properties, Infrared Spectroscopy.
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1. Introduction

Transparent conducting oxides (TCOs) are semiconductors that are produced from a combination of metal and oxygen such as: ZnO, In_2O_3, SnO_2. The studying of TCOs is very important because of their special properties that is used in technology applications [1].

Tin oxide (SnO_2) is considered as one of the most important member of the TCOs for its unique electrical and optical properties because it has low electrical resistivity, high optical transparency in visible region, high optical reflectance in infrared region and chemical inertness. So, SnO2 is used in solar cells, sensor gas, display devices and in other important applications [2].

SnO_2 is an n-type semiconductor with wide band gap energy (Eg = 3.5-4 eV) [3]. SnO_2 has tetragonal structure belonging to the P42/mnm space group. The lattice parameters are a = b = 4.7382 and c = 3.1871 A [4]. 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 [5,6].

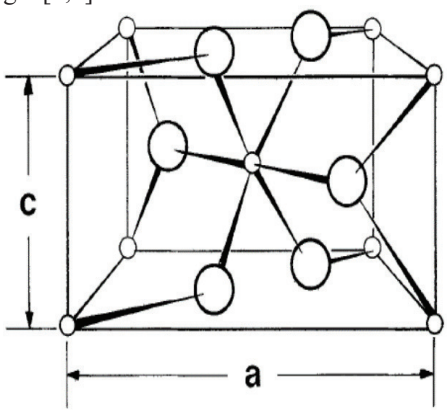


Fig. 1: Unit cell of the crystal structure of SnO_2. Large circles indicate oxygen atoms and the small circles indicate tin atoms.

2 .Experimental Method

$Sn_{1-x}Fe_xO_2$ powders (x = 0.00.0.01,0.03, 0.05, 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 Fe doped SnO_2 powders prepared with various Fe concentration 0 wt%, 1 wt%, 3 wt%, 5 wt% and 6 wt% are shown in Fig. 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 all samples.We noticed disappearance of these orientations (111) ,(210) , (301) in all doped samples.

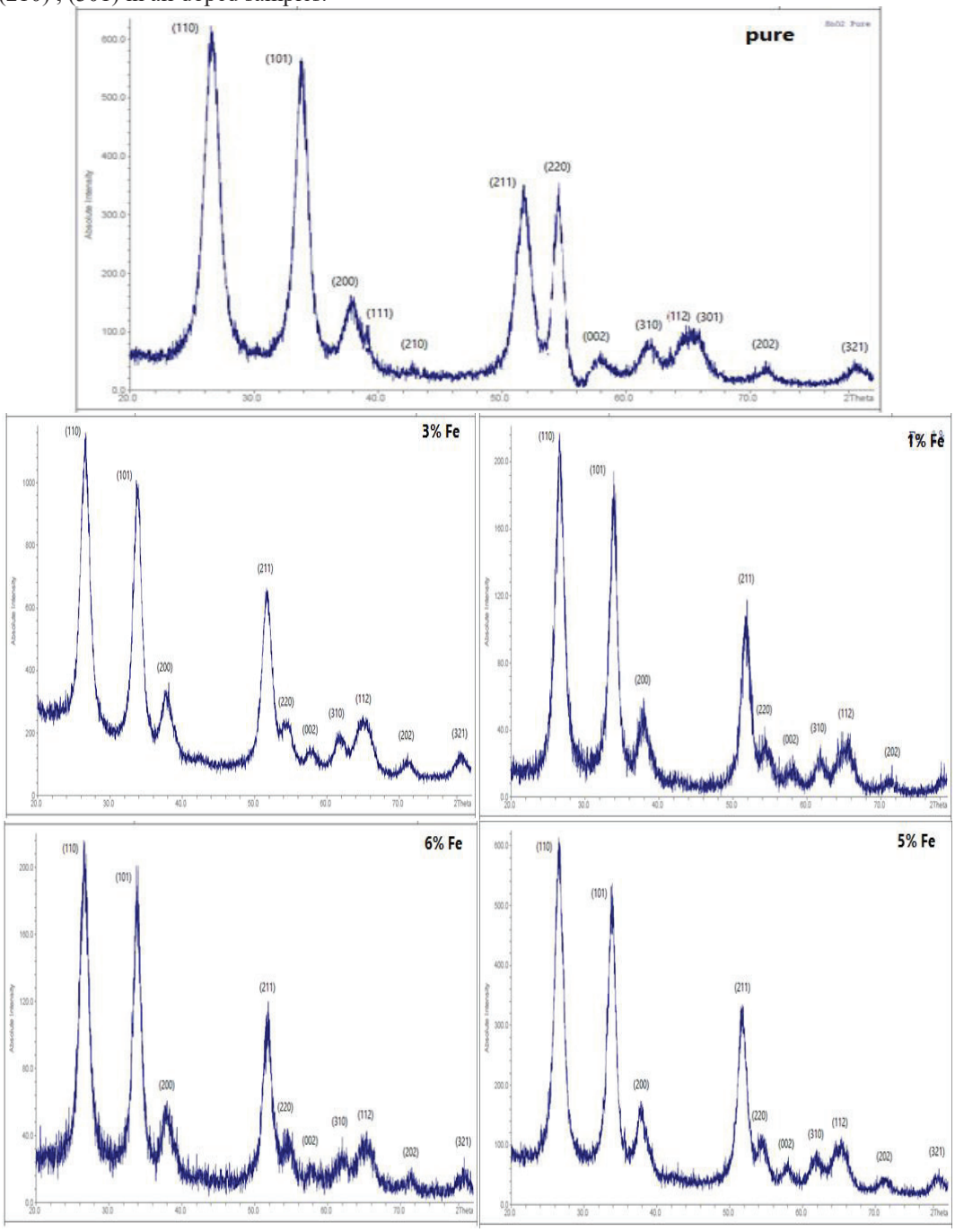


Fig. 2: XRD results of pure SnO_2, 1 wt% Fe doped SnO_2, 3 wt% Fe doped SnO_2, 5 wt% Fe doped SnO_2, 6 wt% Fe doped SnO_2.

Table (1) shows results of structural values of undoped SnO_2 sample.

Table (1)

samples	2θ (deg)	)hkl(	d (A°)	Rel. int. [%]	β (deg)	D (nm)	Average D(nm)	δ 10^{15}line/m^2	Lattice const. a(Å)	Lattice const. c(Å)
SnO_2 pure	26.62	(110)	3.348	100	1.392	6.128	11.877	26.628	4.733	3.185
	33.99	(101)	2.637	87	1.391	6.240		25.680		
	37.95	(200)	2.370	25	0.886	9.908		10.187		
	38.96	(111)	2.311	7	0.440	20.012		2.497		
	42.62	(210)	2.121	4	0.510	17.471		3.276		
	51.87	(211)	1.762	58	1.265	7.297		18.783		
	54.75	(220)	1.676	58	0.506	18.473		2.930		
	57.87	(002)	1.593	11	1.012	9.372		11.385		
	61.99	(310)	1.497	14	1.341	7.221		19.180		
	64.84	(112)	1.437	17	1.898	5.180		37.261		
	65.96	(301)	1.416	15	0.632	15.656		4.080		
	71.25	(202)	1.323	7	1.645	6.207		25.955		
	78.30	(321)	1.221	10	0.424	25.240		1.570		

Table (2) shows results of structural values of Fe doped SnO_2 samples (x=0.01-0.03).

Table (2)

samples	2θ (deg)	)hkl(	d (A°)	Rel. int. [%]	β (deg)	D (nm)	Average D(nm)	δ 10^{15}line/m^2	Lattice const. a(Å)	Lattice const. c(Å)
SnO_2:Fe (1 wt%)	26.50	(110)	3.362	100	1.375	6.202	7.230	25.994	4.755	3.179
	34.01	(101)	2.635	89	1.300	6.677		22.427		
	37.88	(200)	2.375	26	1.500	5.851		29.213		
	51.88	(211)	1.762	53	1.620	5.698		30.803		
	54.38	(220)	1.687	20	1.120	8.332		14.406		
	57.99	(002)	1.590	11	1.300	7.300		18.766		
	61.75	(310)	1.502	18	1.000	9.671		10.693		
	64.70	(112)	1.440	15	1.750	5.614		31.726		
	71.25	(202)	1.323	5	1.050	9.724		10.575		
(3 wt%)	26.50	(110)	3.362	100	1.720	4.958	7.446	40.675	4.755	3.181
	33.98	(101)	2.637	80	1.500	5.787		29.863		
	37.75	(200)	2.382	29	1.500	5.849		29.235		
	51.75	(211)	1.766	57	1.700	5.427		33.956		
	54.37	(220)	1.687	20	1.000	9.331		11.485		
	57.90	(002)	1.592	13	1.000	9.486		11.114		
	61.60	(310)	1.505	18	1.370	7.053		20.100		
	65.12	(112)	1.432	22	1.750	5.627		31.579		
	71.05	(202)	1.326	10	0.950	10.735		8.678		
	78.50	(321)	1.218	11	1.050	10.207		9.599		

Table (3) shows results of structural values of Fe doped SnO_2 samples (x=0.05-0.06).

Table (3)

samples	2θ (deg)	)hkl(	d (A°)	Rel. int. [%]	β (deg)	D (nm)	Average D(nm)	δ 10^{15}line/m^2	Lattice const. a(Å)	Lattice const. c(Å)
(5 wt%)	26.52	(110)	3.360	100	1.500	5.686	7.004	30.932	4.751	3.176
	33.88	(101)	2.645	84	1.370	6.334		24.925		
	37.86	(200)	2.376	29	1.250	7.021		20.289		
	51.88	(211)	1.762	54	1.420	6.500		23.666		
	54.24	(220)	1.691	19	1.250	7.461		17.965		
	58.06	(002)	1.588	12	1.120	8.476		13.920		
	62.06	(310)	1.495	15	1.750	5.535		32.640		
	65.36	(112)	1.427	17	1.750	5.635		31.494		
	71.74	(202)	1.315	7	1.000	10.242		9.533		
	78.54	(321)	1.217	8	1.500	7.147		19.579		
(6 wt%)	26.54	(110)	3.358	100	1.120	7.615	8.074	17.244	4.748	3.184
	33.88	(101)	2.645	87	1.170	7.417		18.179		
	37.98	(200)	2.368	27	1.250	7.023		20.274		
	51.86	(211)	1.762	55	1.250	7.384		18.341		
	54.56	(220)	1.681	20	1.500	6.226		25.796		
	57.90	(002)	1.592	11	1.620	5.855		29.167		
	62.02	(310)	1.496	18	1.250	7.747		16.660		
	64.76	(112)	1.439	20	1.500	6.552		23.293		
	71.34	(202)	1.322	9	0.720	14.189		4.967		
	78.70	(321)	1.215	10	1.000	10.732		8.682		

The relative intensities of undoped and Fe doped SnO_2 powders are calculated. The distance between crystalline planes values (d) are calculated by using following relation:

$$2d.\sin\theta = n\lambda \qquad (1)$$

Where d is distance between crystalline planes (A), θ is the Bragg angle, λ is the wavelength of X-rays (λ=1.54056 A).

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

$$D = \frac{0.94\lambda}{\beta cos\theta} \qquad (2)$$

Where, D is the crystallite size, λ is the wavelength of X-ray, ß is full width at half maximum (FWHM) intensity in radians and θ is Braggs's angle.

The dislocation density is defined as the length of dislocation lines per unit volume and calculated by following equation [2]:

$$\delta = \frac{1}{D^2} \qquad (3)$$

The lattice constants a and c for tetragonal phase structure are determined by the relation [8]:

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \qquad (4)$$

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 A and c= 3.185 A).

The change in peak intensities is basically due to the replacement of Sn^{4+} ions with Fe^{3+} ions in the lattice of the SnO2. This process leads to the movement of Sn^{4+} ions in interstitial sites.

Figure 3 represents variation of the average grain size with different concentrations of Fe doped SnO2 powdres. We observed from tables 1,2,3 that 6 wt% Fe doped SnO2 is the closest value to undoped sample.

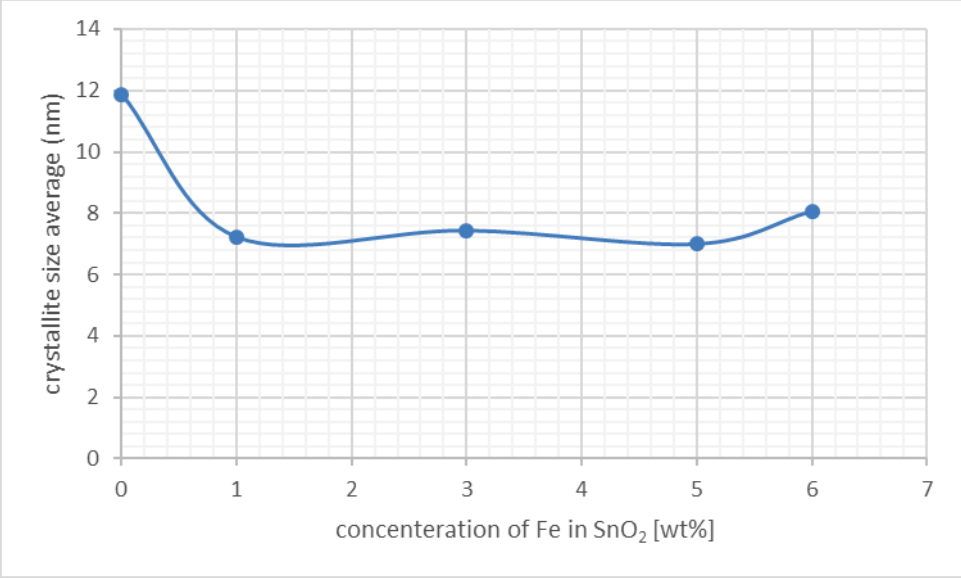
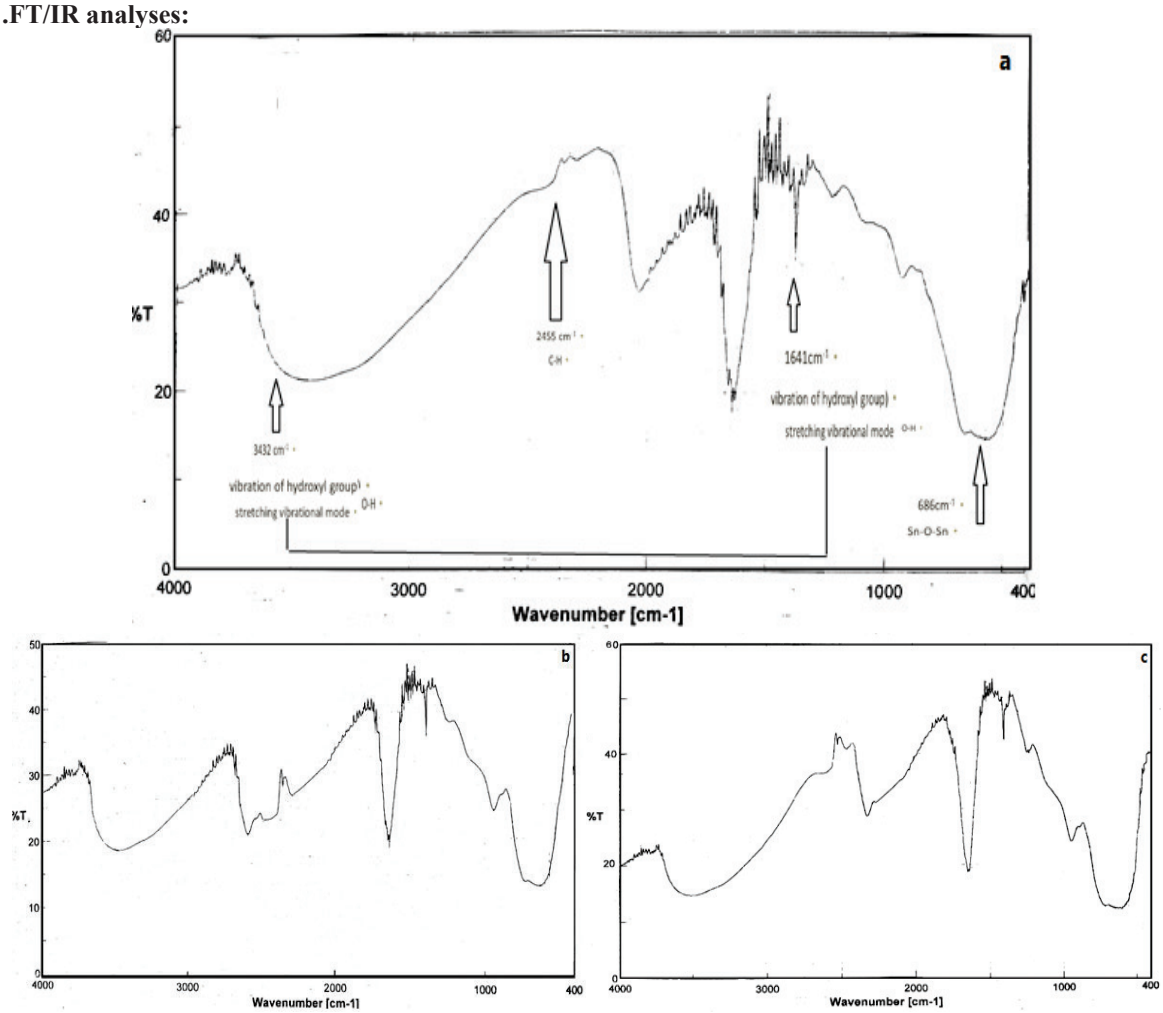


Fig. 3: variation of the average crystallite size with different concentrations of Fe doped SnO_2 powders.

4 .FT/IR analyses:



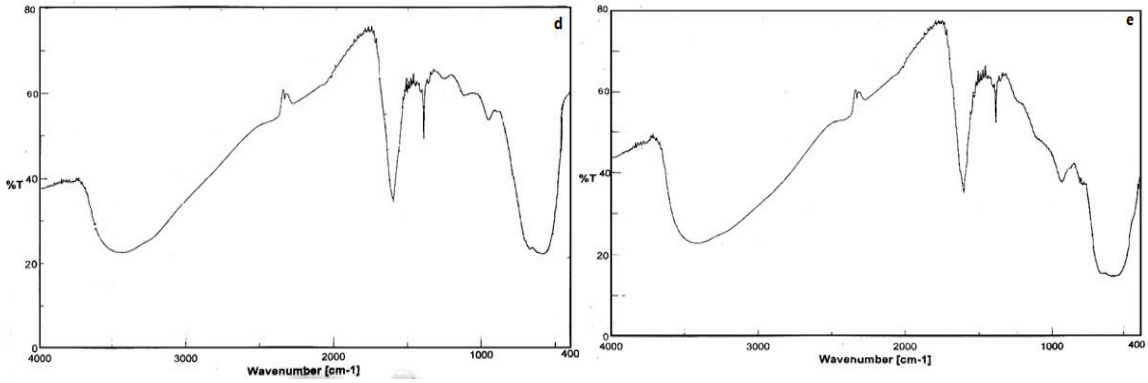


Fig. 4: FTIR analysis of pure and Fe doped SnO_2 powder :(a) pure (b) 1 wt% Fe doped SnO_2, (c) 3 wt% Fe doped SnO_2, (d) 5 wt% Fe doped SnO_2, (e) 6 wt% Fe doped SnO_2

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 [9]. 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 [10]. 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 [11]. The bands observed in the range of 970–700 cm^{-1} are due to the vibration of Sn=O and Sn–O surface cation oxygen bonds [10]. The very strong absorption bands observed in the range of 420–700 cm^{-1} are attributed to the Sn–O antisymmetric vibrations. In that region, the peak at 686 cm^{-1} are assigned to Sn–O–Sn vibrations, respectively [34]. The bands exhibited in the low wave number region 430–620 cm^{-1} are attributed to the Sn–O stretching vibrations [13]. The Fe doping shifts the positions of the absorption bands. It has been previously reported that changes observed in the shape, width, and positions of FTIR peaks are attributed to the variation in the local defects, grain size and shape of the samples [14]. In all samples, the vibrations associated to C–H and O–H bonds are seen. This implies that the surface is highly active and adsorbed these molecules.

5. Conclusion

This paper presents a study of structural properties of Fe 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)، (200)، (111)، (210)، (211)، (220)، (002)، (310)، (112)، (301)، (202) and (321) planes in pure tin oxide sample. The all samples have preferred orientation along (110) plane. The average of crystallite size is within the range [11.877-7.004 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 Fe dopant concentration. FTIR analysis revealed that the Fe doping manifests itself by a shift in Sn–O absorption peaks positions.

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