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Effect of Doping by Mg on the Optical and Structural Properties of SnO_2 Nanoparticles

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ABSTRACT: In this study, the structural and optical properties of Mg doped tin oxide prepared by Sol–gel method ($Sn_{1-x}Mg_xO_2$) nanocrystals were synthesized with *x* ranging between 0, 0.05, 0.1 and 0.15 are reported. The x-ray diffraction data analysis carried out using the Rietveld refinement method shows the formation of only rutile-type structures in all samples, with decreasing of the mean crystallite size.

KEYWORDS: $Sn_{1-x}Mg_xO_2$, Specific surface area, 3D image, Kubelka – Munk function

I. INTRODUCTION:

The preparation of nanoparticles and study its properties are given much importance [1]. Their physical and chemical properties are attracting the present science field when compared with the bulk materials [2]. Tin oxide (SnO_2) is an n-type semiconductor material with rutile tetragonal structure belonging to the $P4_2/mnm$ space group. The lattice parameters are a = b = 4.7382 and c = 3.1871Å, and its band-gap energy in the range between 3.5 and 3.8 eV [3]. Many applications likes, high temperature electron devices, transparent electron devices , sensors for gases detection , solar cells, and flat panel collectors with spectral selective windows ,all this due to its good optical, electrical properties, chemical and thermal stability [4-5]. Many processes have been used for the synthesis of SnO_2 nanostructures, among them sol–gel process has several advantages because of its simplicity, easily control, safety, low cost of the apparatus and raw materials [6&7]. Physical and chemical properties of nanopowder SnO_2 changed by adding some metal ions as a dopant. It is expected to change the charge carriers concentration of the metal oxide matrix, the size of crystallites, and so on. That is due to the diffusion into lattice, nucleation of a second phase or immigration to the interface of the particles [8]. In literature Syed Mansoor Ali most of the dopant likes Cu , Fe , Mn,, Sb, Cs, Ni and F were used to improve the properties of SnO2 thin film, and no one has reported the doping of $Sn_{1-x}Mg_xO_2$ (where x = 0.5, 0.10, 0.15) nanopowder [9]. Magnesium ion concentration in SnO2 suppressed the effective Fermi level (*EF*) which is responsible for the experimentally variation of conductivity [8]. In their calculation Mg-doped SnO_2 P-type conductivity is exhibited and the hole states are located 0.5 eV above the Fermi level, and acts as a shallow acceptor[9].Ferromagnetism at room-temperature was induced by the holes created by Mg on the substitutional site in Mg doped SnO2 [10]. The ionic radius of Mg^{+2} is 0.67Å, close to 0.71Å for Sn^{+4}. So, the replacement of Sn by Mg does not change the crystal structure but it is possible to change its band gap .In this work nanopowder of Mg doped SnO2 synthesis with different concentration and study the effect of doping on the structural parameters and optical properties of the samples by X-ray diffraction (XRD), UV-Vis transmission spectroscopy and atomic force microscopy (AFM).

II. EXPERIMENTAL WORK:

Sol-gel method is used to prepare pure SnO_2 by dissolving 3.5g of Tin (IV) chloride penthydrate (Promchimperm Co,98%,$SnCl_4.5H_2O$) in 100ml of ethanol (Scharlab S.L,99.9%) under vigorous stirring, 4ml of ammonia(India Loba chemie,99%,NH_3OH) was added above the solution drop by drop under stirring. When the reaction completed, an opal gel were filtered and washed with ethanol to remove impurities The obtained powder of tin oxide was annealed in air at 400 and 700℃ .While the Mg doped SnO_2 is performed by using the basic precursors for the preparation of $Sn_{1-x}Mg_xO_2$ (where x = 0.5, 0.10, 0.15), in which $SnCl_4.5H_2O$ and $Mg(NO_3)_2.6H_2O$ (Germany Riedel-DE Haen AG, 99%) are the starting materials followed by the same procedure as for pure SnO2. Finally the obtained powders Mg:SnO_2 were annealed at 700℃.

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III. CHARACTERIZATION:

The obtained powders were carefully subject to the following characterization. Powder XRD pattern was recorded by using SHIMADZU model Japan (6000) diffractometer within the 2θ range of 20 to 80° with Cu-kα radiation of wavelength (λ= 1.5406Å) . The filament current and operating voltage were kept at 30mA and 40kV respectively. The morphology is observed by Atomic Force Microscope (SPMAA 3000 Angstrom Advanced Inc; USA 2008 AFM Contact Mode).The optical properties measured by UV-Vis spectrophotometer (UV-Visible1800, Shimadzu) in the range of 300-900nm.

IV. RESULTS AND DISCUSSION:

XRD analysis:X ray diffraction is non-destructive technique was used to determine the phase crystallinity and structural analysis of the pure and Mg doped SnO_2. The indexing of their diffraction patterns revealed a tetragonal rutile type structure with $P4_2/mnm$ space group as shown in figure (1). In which the diffracted peaks of pure SnO_2 which is annealed at 400℃ agrees very well with tetragonal structure of SnO_2 (JCPDS card no. 41-1445) and with lattice constant a=4.7461Å and c= 3.2106 Å, and for SnO_2 annealed at 700℃ revealed the same peaks angle and an increases in its intensity and decrease in their FWHM. For Mg doped SnO_2 at 700℃ the peaks become wider due to their intensity decreases and shifted to lower diffraction angle with the increases of the Mg concentrations This is due to the substitution of Sn^{+4} ions at the lattice sites with the Mg^{+2} ion. The lattice parameters of SnO_2 decreased after Mg doping as shown in (Table 1). The observed variation in lattice parameters is consistent with the smaller radius of the Mg^{+2} ion. For the tetragonal structure, lattice parameters can be calculated from:

$$1/d_{hkl}^2 = h^2 + k^2/a^2 + l^2/c^2$$

Where h, k, and l are all integers, (hkl) is the lattice plane indices, a and c are lattice constants. The crystallite size (D) of undoped and Mg doped SnO2 powder for all the dopant samples were calculated using Debye-Scherrer formula [11]:

$$D = k\lambda/\beta \cos\theta$$

Where k is a constant, λ is the diffraction wavelength of Cu Kα (λ = 1.5406 Å), β is the full width at half maximum (FWHM), and θ is the angle of diffraction. Then, using Williamson-Hall in order to calculate crystallite size and strain [12]:

$$\beta \cos\theta = (k\lambda/D) + 4\varepsilon \sin\theta$$

Where ε the internal strain and k is a constant equals to 0.9. The density of powder $\rho_{X\text{-}ray}$ was calculated from x-ray data by using this equation [13]:

$$\rho_{X\text{-}ray} = Z\, M_{wt}/V\, N_a$$

Where ρ: density (g/cm^3), M_{wt}: molar mass (g/mol), Z: the number of lattice points/unit cell, V in (cm^3) and Na: Avogadro number (1/mol)

The specific surface area calculated by following equation [14]:

$$SSA = 6*10^3/D\, \rho_{X\text{-}ray}$$

Dislocation density (δ) and number of unit cells (n) are calculated using the relations [15,16]:

$$\delta = 1/D^2$$

$$n = \pi D^3/6\, V$$

All calculated values are presented in table 1.

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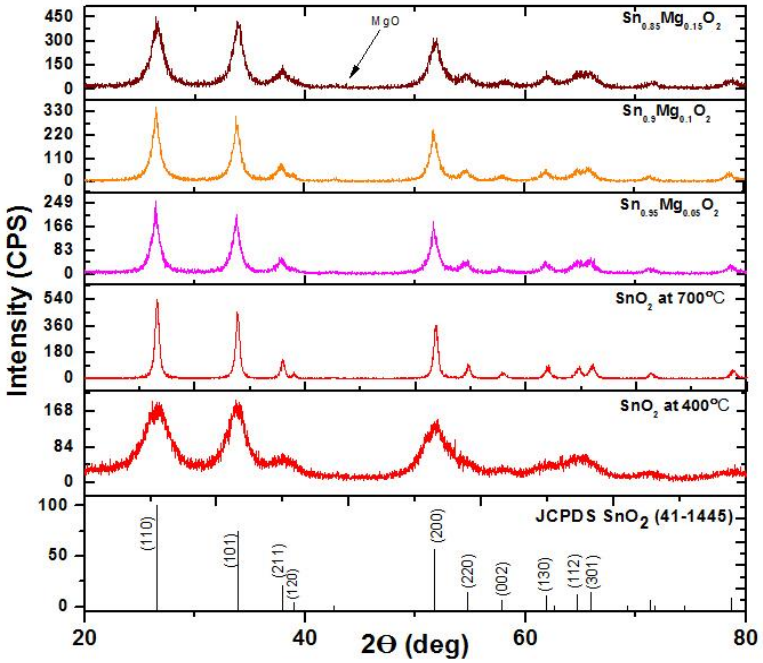

Fig 1: XRD pattern for prepared pure at 400,700°C and Mg doped SnO_2 nanoparticles

Table 1: shows grain size by Debye-Scherrer equation and W-H, lattice parameter, X-ray and dislocations density, Specific surface area, and number of unit cells

Sample	400°C	700°C	700°C		
	Pure SnO_2		$Sn_{0.95}Mg_{0.05}O_2$	$Sn_{0.9}Mg_{0.1}O_2$	$Sn_{0.85}Mg_{0.15}O_2$
D_{D-S} (nm)	3.62	18.39	11.42	10.19	7.356
D_{W-H} (nm)	3.84	18.244	10.35	8.56	6.22
ε	-0.00623	-0.001	0.00018	-0.0031	-0.0025
a=b (Å)	4.7461	4.7487	4.74638	4.74376	4.74224
c (Å)	3.2106	3.18812	3.19045	3.1851	3.17985
V(Å^3)	72.3202	71.89259	71.79128	71.67495	71.51108
ρ_{Xray}(g/cm^3)	6.92	6.962165	6.97199	6.983305	6.9993
SS.A (m^2/g)	239.518	46.866	75.358	84.318	116.535
δ(1/m^2)*10^{16}	7.63	0.328	0.85575	1.0555	2.079
n	343.2768	45288.6	10862.39	7729.55	2914.41

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From table1,the calculated grain size of pure SnO_2 for 400C about 4 nm which are grown to 18nm after at 700C.While for doped samples with 0.05 Mg it decrease to 11 n m at 700Cad further decreases as doping concentration increases for each of Debye-Scherrer and Williamson-Hall. Lattice parameters approximately the same for all samples. Specific surface area increases from 75 m2/g at 0.05 Mg to 116 m2/g at 0.15 this Surface excess in MgO doped SnO_2 nanoparticles is an important indication to the system's energetics and size stability of the nanoparticle.

Atomic force microscope (AFM) analysis: Atomic force microscopy (AFM) is a useful technique to determine the surface morphology and particle size of the samples. Figure 2 show the 2D and 3D AFM images and particle distribution of pure and Mg doped SnO_2. Its images for pure and doped SnO_2 nanoparticles revealed semi-spherical shapes, their particle distribution is uniform and particle size reduces with the increasing of the Mg concentrations. Roughness decreases with increases of doping concentration. The size of the particles obtained from (AFM) images is the largest to those values obtained from measurements of (XRD) due to the one consists of crystallite, and your (AFM) photographed the top surface of the granules either apparatus (XRD) gets diffraction from surfaces of crystalline which are each a crystallization of microscopic size. Average grain size, roughness, square root, average rate of rise of the prepared samples values are shown in table 2.

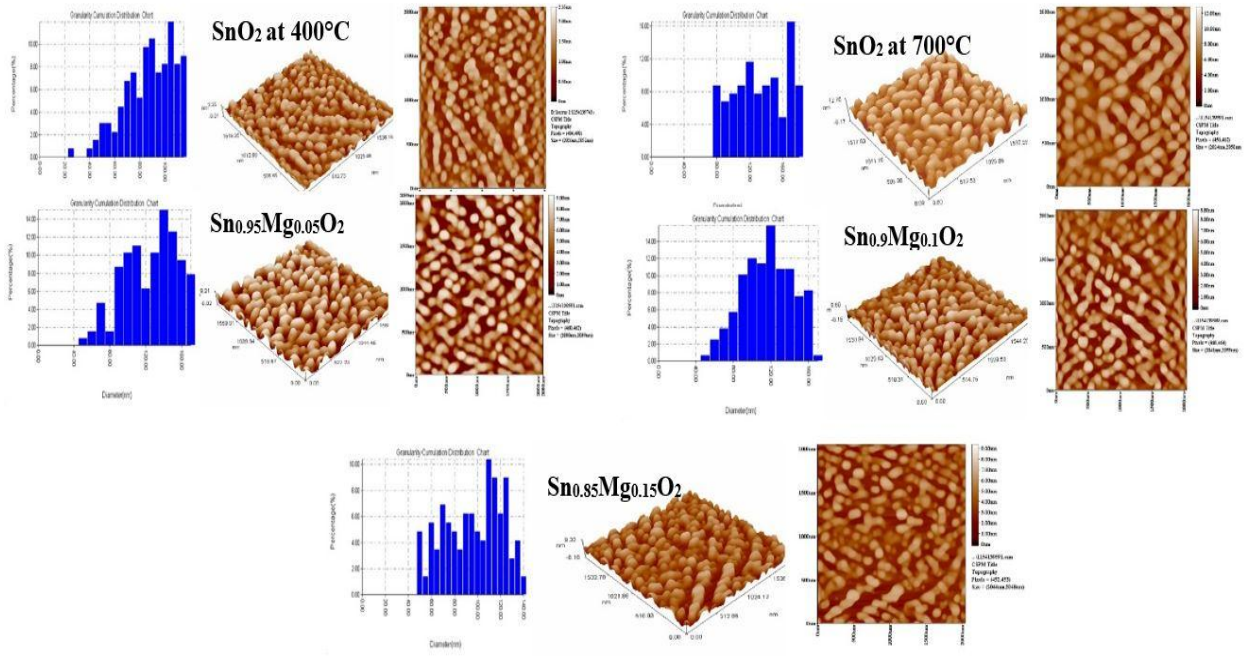

Fig 2: AFM 2D,3D image and the particles distribution

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Table 2: Results of The AFM images morphology characteristics with of pure and doped SnO_2 NPs

Sample		Avg. diameter (nm)	Ave. Roughness (nm)	RMS (nm)
SnO_2 at 400°C		85.27	0.332	0.381
700°C	SnO_2	127.71	1.6	1.85
	$Sn_{0.95}Mg_{0.05}O_2$	120.38	1.98	2.28
	$Sn_{0.9}Mg_{0.1}O_2$	111.24	1.36	1.58
	$Sn_{0.85}Mg_{0.15}O_2$	94.04	1.18	1.35

UV–Vis spectra analysis: In order to the study of the optical properties of nanoparticles, we dissolved 0.025M of nanopowder in 5ml of double distilled water. Then the solution was put in ultrasonic for 5 minutes. The reference sample is double distilled water and the tin oxide sample which was dissolved in double distilled water, were put in Absorption Spectrometer. First, of the work is to omit the water absorption and then calculated the absorption of nanoparticles. The absorbance spectra of pure and Mg doped SnO_2 nanoparticles are depicted in figure 3. From the absorbance data the Transmission and Reflectance were calculated for certain wavelength .The band gap energies calculated according to Kubelka – Munk (K-M) model [17]. The K-M model at any wavelength is given by equation:

$$F(\infty) = (1-R)^2/2R$$

F(∞) is the so called remission or Kubelka – Munk f unction where R is the percentage of reflectance [18]. A graph is plotted between $[F(\infty)h\upsilon]^2$ Vs hν and its intercept with hν represent the band gap energy [19].

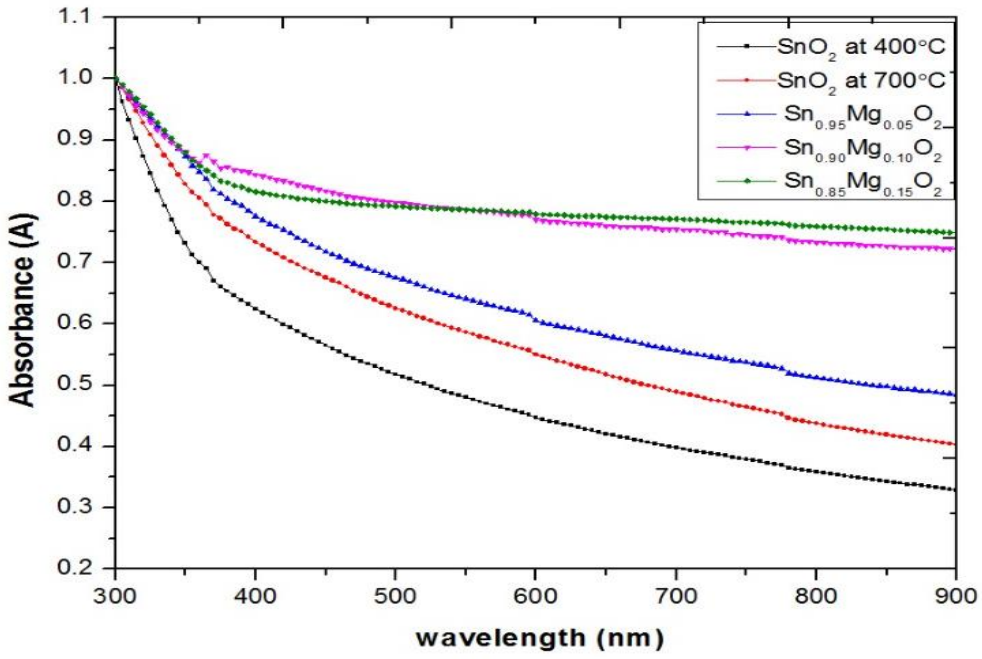

Fig 3: absorbance spectra with wavelength of pure and Mg doped SnO_2

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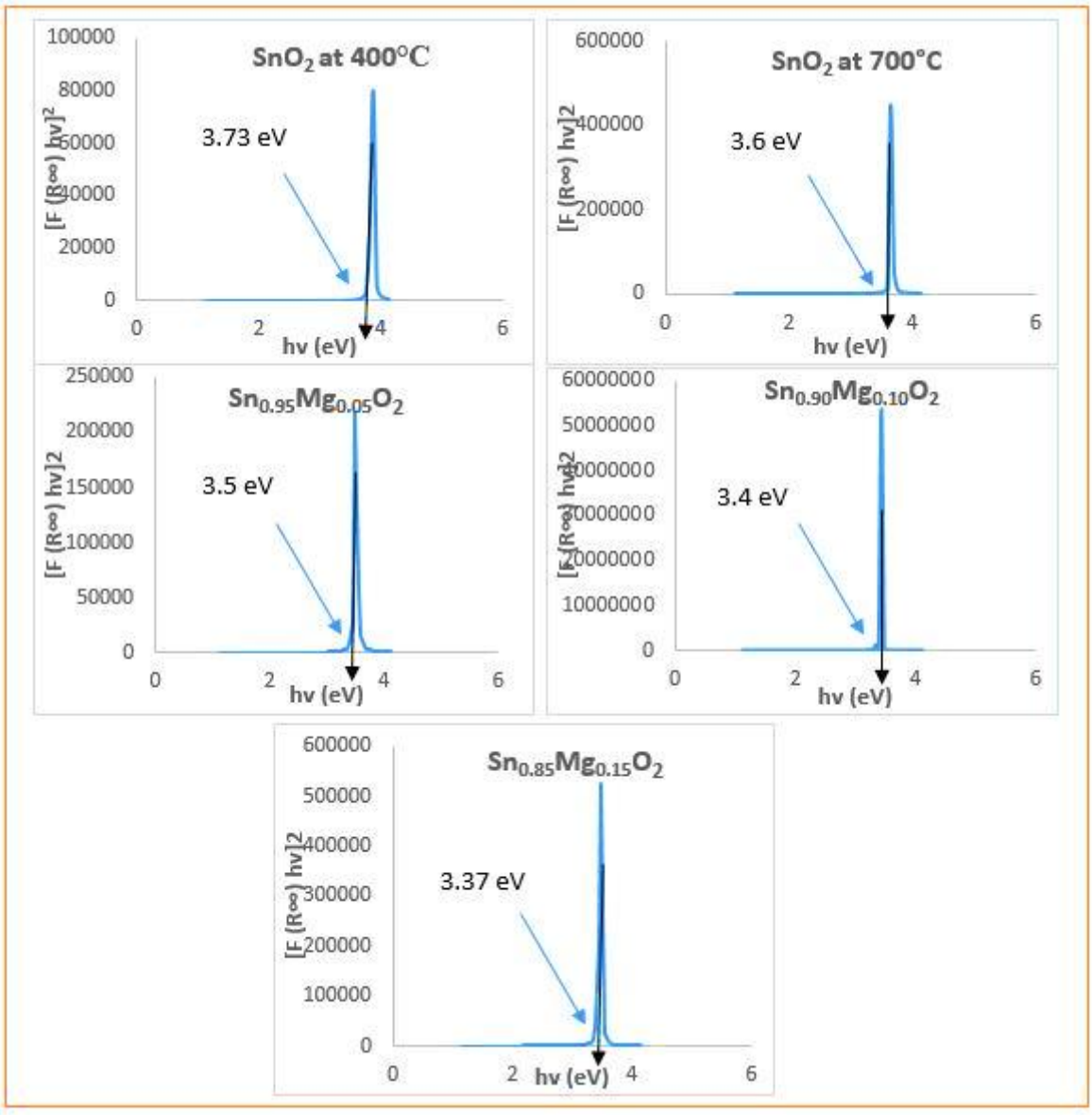

Fig 4: Show the direct energy gap for pure and Mg doped SnO_2

From figure 4 the absorbance increase proportionally with increase doping concentration. Direct energy gap decreasing by increase annealing temperature [20], also it decrease with increase mg dopant concentration The observed decrease in band gap energy confirms that Mg^{+2} ion substituted in SnO_2 host lattice. Similar findings were observed in Mg doped SnO_2 thin films [21].

V. CONCLUSIONS:

Pure and doped nano crystalline SnO_2 powders were successfully synthesized via a simple sol-gel. The size of particles increase by increase annealing temperature and decrease by adding Mg as a dopant, dislocation density and

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specific surface area increase with doping and unit cells increases in addition of lattice parameter direct band gap decrease by increase doping concentration. Surface roughness decrease with increase doping and the energy band gap decrease with increase of doping.

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