

The tin doping effect on the physicochemical and nonlinear optical properties of the manganese oxide (Mn_3O_4 : Sn) thin films

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Abstract. Undoped and tin doped manganese oxide, $\text{Mn}_{3-x}\text{Sn}_x\text{O}_4$, ($x=0, 2$, and 4 at %) thin films were successfully elaborated by the chemical route defined in the spray pyrolysis technique and deposited on glass substrates at a temperature of 350°C . The physicochemical characterization of the thin films was performed using an X-ray diffractometer (XRD) that showed a polycrystalline tetragonal structure for all thin films. Raman measurement confirmed the vibrational mode, A_{1g} , and the XRD results with the presence of no secondary phases. Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy depicted the surface morphology and the elemental composition (Mn, O, and Sn) of the elaborated thin films. Finally, the optical analysis was carried out, and it showed an increase in the average transmittance of the Mn_3O_4 : Sn ($0, 2$, and 4 at %) from 57.6% to 62.2% for 700 nm and an increase of their optical band gap from 3.27 eV to 3.61 eV . We note also a decrease of their dispersive energy parameter E_d from 5.44 eV to 4.86 eV , of their static refractive index n_0 from 2.02 to 1.86 , as well as for their nonlinear optical parameters presented by the nonlinear refractive index n_2 from $1.14 \cdot 10^{-11}$ to $0.51 \cdot 10^{-11}$ and the third order susceptibility χ^3 from $6.14 \cdot 10^{-13}$ esu to $2.49 \cdot 10^{-13}$ esu. These values can be correlated to the poor crystallinity and the tensile strain of the Mn_3O_4 : Sn ($0, 2$, and 4 at %) thin films, as well as to the high order of the optical bandgap energy and the decrease of the linear refractive index of these films. Hence, these thin films can be used as material for nonlinear optical applications.

1 Introduction

Transition metal oxides (TMO) are part of transparent conducting oxides (TCO) which held important place in multiple domains due to their optical and electrical properties. Among those TMO, manganese oxide is a metal oxide semiconductor that has been used in a variety of applications and domains such as energy storage, batteries and supercapacitors [1], gas sensors [2], high-density storage devices [3], optoelectronics [4], etc. Manganese oxide is present in several phases, such as MnO , MnO_2 , Mn_2O_3 , and Mn_5O_8 , each one with its own unique electrical and optical properties.

In order to enhance and tailor the optical and electrical properties of the Mn_3O_4 intrinsic characteristics, different doping elements and methods were used. Some of these elements are lithium [5], nickel [4], cobalt [6], zirconium [7], and copper [8]. The Mn_3O_4 was elaborated by different techniques to enhance its properties, such as SILAR pyrolysis [8], Sol-gel, chemical vapor deposition [9], spray pyrolysis [10], electron beam evaporation [11] etc.

In this study, we deposited the undoped and tin-doped Mn_3O_4 ($0, 2$, and 4 at %) thin films on glass substrates using the spray pyrolysis technique, which is one of the most simple and low-cost techniques offering a uniform deposition area with good optical and conductivity properties. The obtained thin films were subjected to different characterization techniques. First, X-ray diffraction and Raman spectroscopy were used for a structural characterization, followed by a scanning electron microscope for surface morphology and an EDS analysis for the quantitative identification of elements. Finally, optical characterization was used to investigate the linear and nonlinear responses of the undoped and tin-doped Mn_3O_4 thin films.

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2 Materials and methods

2.1 Material synthesis

Undoped and tin-doped manganese oxide, Mn_3O_4 : Sn, thin films (0, 2, and 4 at %) were elaborated by a chemical route presented in the spray pyrolysis technique that has been described in [12]. The sample preparation began with dissolving a calculated mass of Manganese (II) Chloride Tetrahydrate MnCl_2 in $4\text{H}_2\text{O}$ for a concentration of 0.1 M and a different ratio of Tin dichloride SnCl_2 as a dopant element (0, 2, and 4 at %) After obtaining a homogeneous solution by stirring, the solution volume of 30 ml was carried out by a flow meter to a nozzle to be pulverized for 8 minutes on a 350°C preheated clean glass substrate. These glass substrates were previously subjected to a cleaning processor described as follows: acetone, ethanol, and diluted hydrochloride (HCl) acid for 5 minutes each under agitation, and between each step, washed them with distilled water.

2.2 Material characterization

The structural characterization of the undoped and tin doped manganese oxide (0, 2, and 4 at %) thin films were proceed by an X-ray diffraction “XRD” system, “D8 Advance Eco” provided from “Bruker”, with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The X-ray generator’s power was 1000 W (40 KV, 25 mA), for a scan range from 15° to 70° . Raman spectroscopy also provided from “Bruker”, model name “Senterra”, with a diode laser source fixed at a wavelength of 532 nm. Field Emission Scanning Electron Microscope (HRFESEM) coupled with Energy Dispersive X-ray “SEM-EDS” spectroscopy, ZEISS GeminiSEM 500, was used for the surface morphology and chemical elements characterization and analysis. Finally, the optical characterization was carried out by an *UV-Vis-NIR* spectrophotometer model name “UV-3600i plus” purchased and provided by “Shimadzu”, the analysis where carried in the wavelength range from 300 nm to 1600 nm.

3 Results and discussions

3.1 X-ray diffraction “XRD” study

The structural characteristics of the elaborated undoped and tin doped manganese oxide, Mn_3O_4 : Sn (0, 2, and 4 at %), thin films were investigated by an X-ray diffraction characterization. The XRD characterization of these thin films were carried out in a range of 2θ from 15° to 70° . Hence, the results of their structural characterization are illustrated in figure 1.

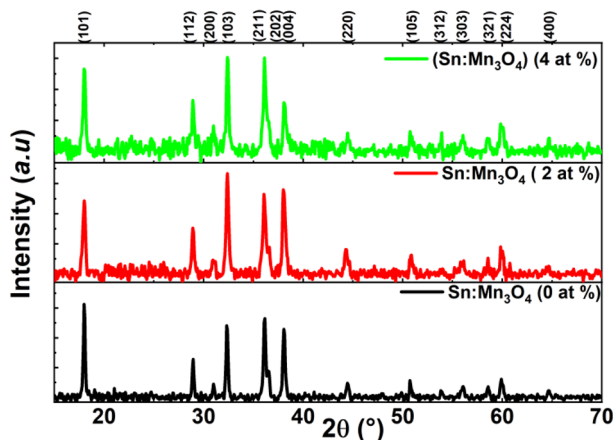


Fig. 1: X-ray diffraction peaks of Mn_3O_4 : Sn (0, 2, and 4 at %) thin films.

The XRD patterns presented in figure 1 (a, b, and c) are compared to a referential peaks provided by the Joint Committee on Powder Diffraction Standards, JCPDS, card number 01-080-0382. Through the juxtapositioning of these peaks, a conclusion is draw that the Mn_3O_4 : Sn (0, 2, and 4 at %) thin films are crystallized in a tetragonal hausmannite structure (Space group I41/amd). Also, no secondary phases are observed in figure 1 originating from manganese oxide variable degrees of oxidation nor from tin-manganese alloys. This allow us to assume the successful substitution of manganese with tin into the Mn_3O_4 lattice.

As can be seen, all elaborated thin films have a polycrystalline texture with the following major plans (101), (112), (200), (103), (211), (202), and (004) corresponding to the 18°, 28.9°, 36°, 36.4°, 38°, and 44° respectively. Due to tin doping, a slight shift of the peaks with the disappearance of the (202) plan as the tin doping increased. The shift of the peaks in Mn₃O₄: Sn (2 and 4 at %) thin films is an evidence for a successful substitution of the Mn³⁺ ions with Sn⁴⁺ ions. At first hand, we proceed by obtaining the values of the lattice parameters of the Mn₃O₄: Sn thin films. They were estimated from the standard relation of the tetragonal structure [1]:

$$\frac{1}{d_{hkl}^2} = \frac{(h^2+k^2)}{a^2} + \frac{l^2}{c^2} \tag{1}$$

With a, b, and c are the lattice parameters and dhkl is the inter-planary distance with the h, k, and l are miller indices. Secondly, the average crystallites size, D, and the micro-strain, ε, were investigated using two different routes, first route has been described by the Scherrer equation and the second route obtained through the Williamson-Hall method, respectively [10,13,14]:

$$D = \frac{0.9 \lambda}{\beta \cos(\theta)} \tag{2}$$

$$\varepsilon = \frac{\beta \cos(\theta)}{4} \tag{3}$$

$$\beta \cos(\theta) = \varepsilon (4 \sin(\theta)) + \frac{\lambda B}{D} \tag{4}$$

With, β the full width at the half maximum FWHM (rad), λ (Å) the wavelength of the incident X-ray beam of Cu Kα, θ (rad) the angle value of the selected diffraction peak and finally, B shape factor valued (0.9). The structural parameters of the Mn₃O₄: Sn (0, 2, and 4 at %) thin films are calculated and presented in table 1 as follow:

Table 1. Mn₃O₄: Sn (0, 2, and 4 at %) thin films structural parameters

Mn ₃ O ₄ : Sn (at %)	a(Å)	c (Å)	D (nm)	ε 10 ⁻³ (a.u)	D _{W-H} (nm)	ε _{W-H} 10 ⁻³
0	5.766	9.416	22.42	1.547	28.55	1.78
2	5.778	9.415	20.157	1.721	25.936	2.14
4	5.769	9.438	19.958	1.738	25.792	2.08

On the one hand, table 1 and equation 1 show a similarity of the lattice parameters a and c between the calculated ones for the undoped Mn₃O₄ and the ones provided in the JCPDS card 01-080-0382 (a = b = 5.765 and c = 9.442). On the other hand, the lattice parameters of the tin-doped manganese oxides (2 and 4 at%) showed an increase compared to the undoped Mn₃O₄, as presented in table 1. This action is due to the different radius between Mn³⁺ (0.65 Å) ions and the Sn⁴⁺ (0.69 Å) ions. A similar behavior was observed by et al. when they doped the Mn₃O₄ with tin ions and the lattice volume expanded through the increase of the lattice parameters resulting from the substitution of Mn³⁺ (smaller ionic radius) with Sn⁴⁺ ions (bigger ionic radius) [15]. Also, this variation can be taken as a second piece of evidence for the substitution of Mn by Sn ions. The average crystallite size and micro-strain effect are subjects of investigation by the Williamson-Hall equation that have been described by Rossi et al. [13]. Figure 2 presents the plots of β cos (θ) as a function of 4 sin (θ) of the Mn₃O₄:Sn (0, 2, and 4 at %) thin films.

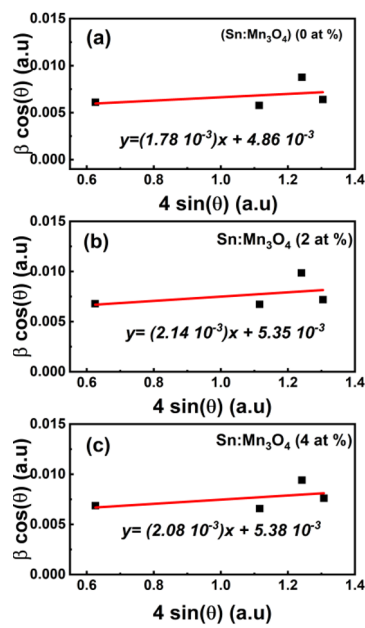


Figure 2: (a-c) Williamson-Hall plots of Mn₃O₄: Sn (0, 2, and 4 at %) thin films respectively.

The extracted values of the crystallite size and strain from these plots (Figure 2) are shown in table 1. Starting with the average crystallite size, its value decreases as the doping concentration increases, and it is validated by both methods. The crystallite size reduction from 22.42 nm (0 at%) to 19.958 nm (4 at%) can be assigned to the increase of tin ions in the Mn₃O₄ matrix, pushing the nucleation and growth of the nanocrystals to be prevented [12]. Further, the strain parameter exhibits a positive increase as a function of the doping rate of tin in the Mn₃O₄ lattice. The positive value signs for a tensile strain behavior; this can be possible and correlated to the increase of the lattice parameters. Furthermore, the strain is directly proportional to the stress, and the increase of this last can cause a disturbance in the crystallite growth kinetics, resulting in a decrease in the average crystallite size [16].

3.2 Raman spectroscopy study

Raman analysis is a characterization technique used to complete and verify the structural findings obtained by the XRD (Figure 1 and 2). It allows an accurate readings of the all local structures presents in the Mn₃O₄: Sn (0, 2, and 4 at %) thin films that might have been undetectable by the XRD characterization.

Figure 3 shows the Raman responses of the Mn₃O₄: Sn (0, 2, and 4 at %) thin films plotted in the range of 100 to 1000 cm⁻¹.

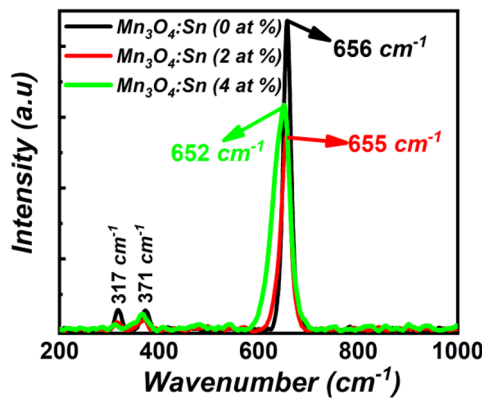


Figure 3: Raman spectroscopy of Mn_3O_4 : Sn (0, 2, and 4 at %) thin films.

The Raman plots of the Mn_3O_4 :Sn (0, 2, and 4 at%) thin films exhibits one intense peak and two smaller ones at 656 cm^{-1} , 371 cm^{-1} , and 317 cm^{-1} respectively. The Raman peak at 656 cm^{-1} correspond to the A_{1g} mode belonged to the motion of oxygen ions inside the MnO_6 octahedral, as for the 371 cm^{-1} and 317 cm^{-1} peaks they are related to the Mn-O bending modes and the asymmetric stretch of bridge oxygen (Mn-O-Mn) respectively [17,18]. Also no presences for secondary phases or alloys were detected in figure 3. Further, through the work of Liang et al. [19] the Raman peak shifting, red or blue shifts, can be caused by the nature and presence of the strain into the thin films. Where the redshift observed in figure 3 for the Mn_3O_4 : Sn (0, 2, and 4 at%) are linked to the tensile strain that was coming from the introduction of Sn dopant element in Mn_3O_4 matrix (XRD section) which lead to an increase in the bond length hence a decrease of the force constants in the Mn_3O_4 : Sn (0, 2, and 4 at%) thin films. Furthermore based on Kocyigit [20] work on the relation between the full width at half maximum of the Raman major peak and the crystallinity of the sample under investigation where the increase of the FWHM signified a decrease in crystallinity and vice versa. Hence based on the increase of FWHM of 657 cm^{-1} major peak of all three thin films implies a decrease of the cristallinity as the dopant concentration increases.

3.3 Morphological properties

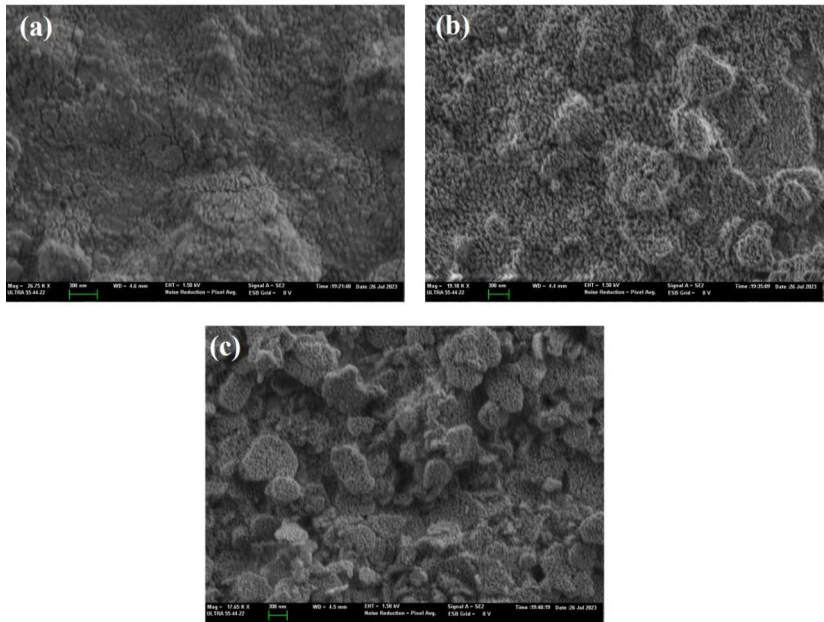


Figure 4: (a-c) SEM images of Mn_3O_4 : Sn (0, 2, and 4 at %) thin films respectively.

The SEM images of the undoped and tin doped Mn_3O_4 (0, 2, and 4 at %) thin films were taken with an acceleration voltage of 1.5 KV, a zoom in of 300 nm, and a magnitude of 26.75Kx, 19.18Kx, and 17.65Kx respectively. In Figure 4 (a–c), a variation in the surface morphology has appeared as the tin doping concentration introduced to the Mn_3O_4 lattice increased. It is noticeable that the agglomeration of grains occurred with the increase of tin insertion in the Mn_3O_4 lattice. Also due to the grains agglomeration effect, an increase in the surface area as depicted in figures 4 (a–c) is observed, resulting in an increase in the surface roughness of the Mn_3O_4 : Sn (0, 2, and 4 at %) thin films, which will negatively impact on the nonlinear response of the third-order susceptibility as it will be discuss in the optical section.

Figure 5 displays the chemical components of the undoped and Sn doped Mn_3O_4 (0, 2, and 4 at%) plots through the EDX analysis. Tin, Oxygen, and Manganese are all presented, and the molar ration Mn/O in all films is shown to be extremely near to the nominal composition of Mn_3O_4 , which confirmed the Mn_3O_4 tetragonal structure for all the films.

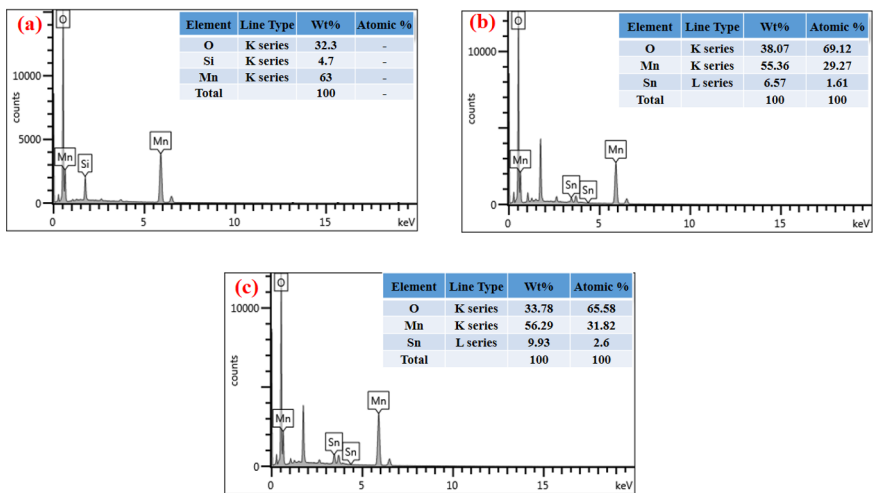


Figure 5: (a-c) Energy dispersive X-ray analysis of Mn₃O₄: Sn (0, 2, and 4 at %) thin films respectively.

3.4 Optical properties

Both the transmittance and reflectance of the undoped and tin doped manganese oxide (0, 2, and 4 at %) thin films are illustrated in figure 6 (a and b) respectively.

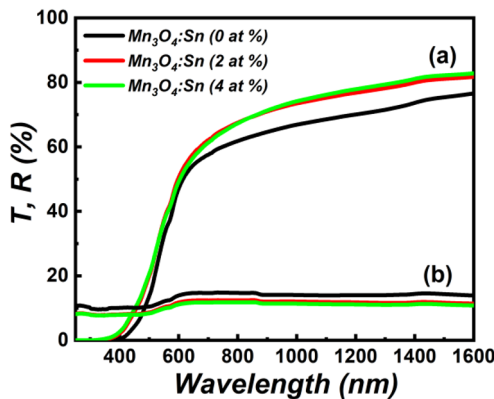


Figure 6: a-b, transmittance and reflectance plots of undoped and tin doped Mn₃O₄ (0, 2, and 4 at %) thin films respectively.

The transmittance average for the undoped Mn₃O₄ thin film was between 50 and 60% in the visible spectrum, specifically 57.6% for a wavelength of 700 nm and also 70% for the 1064 nm wavelength, which corresponds to the excitation wavelength of the Nd/YAG laser. These values are in good agreement with the ones found in literature [21]. For the tin doped Mn₃O₄ thin films, the transmittance value increases from 57.6 % to 62 % (2 at % of Sn) to 61 % (4 at % of Sn) in the 700 nm and from 70 % (0 at % of Sn) to 74.6 % (2 at % of Sn) to 75.5% (4 at % of Sn) in the 1064 nm wavelength.

The absorbance data were used to calculate the absorption coefficient, which will be used to obtain the band gap energy of the Mn₃O₄: Sn (0, 2, and 4 at %) thin films through the Tauc model that was described by Rossi et al. [13]. The equation of the Tauc model is the following:

$$\alpha h\nu = D (h\nu - E_g)^{n3} \tag{5}$$

With α the absorption coefficient, $h\nu$ the photon energy, D a constant, E_g the band gap energy, and $n = 0.5$ or 2 for direct or indirect band gap, respectively. Hence, the band gap energy of the elaborated thin films was extracted from the plots that are presented in figure 7. The obtained values are 3.27 eV, 3.59 eV, and 3.61 eV for the Mn₃O₄: Sn (0, 2, and 4 at%), respectively. The high value obtained for the undoped Mn₃O₄ compared to the 2.8 eV can be explained by the

quantum confinement effect described in the small size of the crystallite (XRD section), the same behavior is described by Hosny et al. [22]. The increase in the E_g for the tin doped manganese oxide can be corroborated with the Burstein-Moss effect, where an increase in the carrier electrons by the tin introduction leads the Fermi level to merge into the covalent band [13]. The conduction band becomes significantly filled and the lowest energy states of it are blocked, hence the absorption inter-band reach out to higher energy states and the blue shift occurs [23].

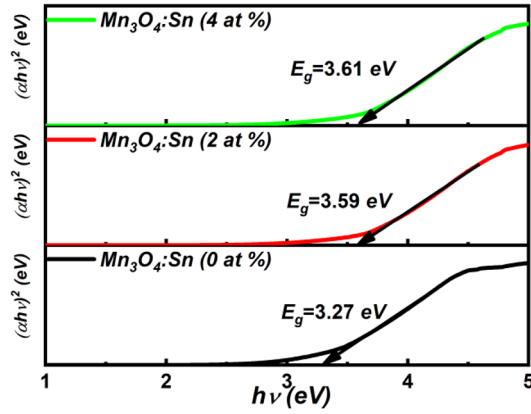


Figure 7: optical band gap energy of the undoped and tin doped Mn_3O_4 (0, 2, and 4 at %) thin films.

The reflectance data was held useful to calculate the refractive index of the undoped and tin doped Mn_3O_4 (0, 2, and 4 at %) thin films through the following equation [24] :

$$n = \frac{1-R}{1+R} + \left(\frac{4R}{(1-R)^2} - k^2 \right)^{\frac{1}{2}} \quad (6)$$

Where n the refractive index, R the reflectance, and k is the extinction coefficient described as follow $k = \frac{\alpha\lambda}{4\pi}$ with α the absorption coefficient and λ wavelength.

The refractive index in figure 8 (c) displays the same trend as the reflectance plot of $Mn_3O_4:Sn$ (0, 2, and 4 at %). The refractive index increases from 300 nm to reach a maximum at 600 nm and then stays at approximately at the same value until it reaches 1600 nm. This behavior is noticeable for all doped thin films and it's an important factor, the static of the refractive index, which allows him to be used in different domain of applications such as optical filters, frequency-cutter, modulation, and switches [25]. These findings of refractive index are higher than the ones existing in literature. Pandey et al. [25] have obtained a refractive index of 1.77 for Mn_3O_4 thin films prepared by the sol-gel technic. Alduwaib et al. [21] have obtained a refractive index value of 1.39 for 550 nm and increases to 1.58 as the wavelength increases for the Mn_3O_4 thin films prepared by the spray pyrolysis technic. Finally, Panday et al. [26] through the spin-coating technic have elaborated Mn_3O_4 thin films where the refractive index was 1.5 in the visible region.

As for the extinction coefficient, this factor has the same analogy as the absorbance coefficient, where a blue shift is observed for the tin doped thin films compared to the undoped one. Also, the decrease of the 'k' for the tin doped Mn_3O_4 films compared to the undoped one can be related to the increase of the band gap energy due to the incorporation of tin ions into the Mn_3O_4 lattice [27].

Both the n and k parameters take part in describing the complex dielectric component through the following equations [24]:

$$\varepsilon' = k^2 + n^2 \quad (7)$$

$$\varepsilon'' = 2nk \quad (8)$$

As illustrated in figure 8 (a and b) both the ε' and ε'' present the same plots as the n and k parameters. Thus the ε' shows an increase until the 600 nm wavelength, then stabilizes at the visible and near infrared regions (1600 nm). The tin insertion seems to decrease the value of the real and imaginary parts of the dielectric constant. The ε'' values are smaller than ε' , which implies a small energy loss of light through the thin films.

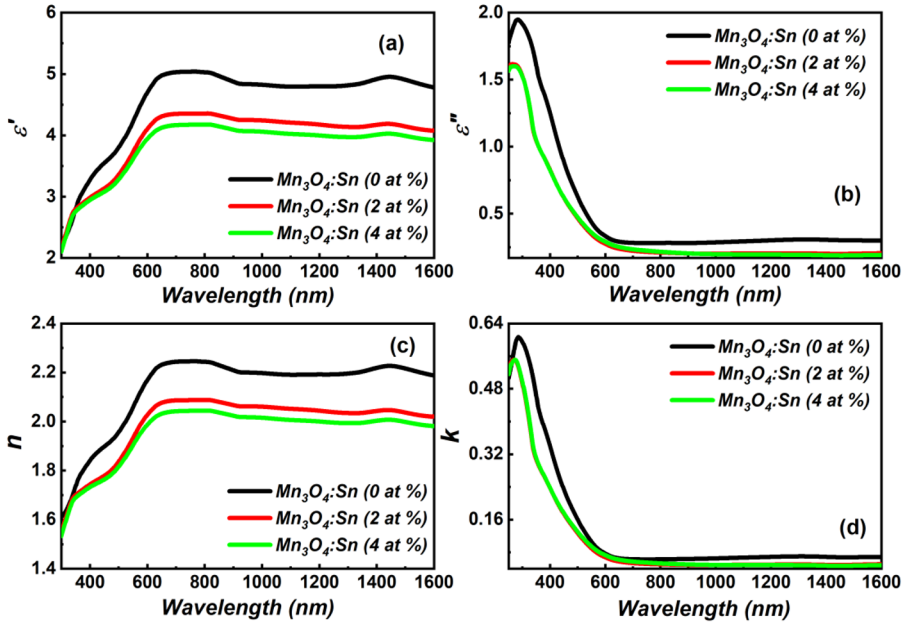


Figure 8: (a-d), real and imaginary part of complex optical dielectric constant and refractive index of undoped and tin doped Mn_3O_4 (0, 2, and 4 at %) thin films respectively.

Furthermore we adopted the Wemple-DiDomenico, WDD, single oscillator model to examine the static refractive index and the high-frequency dielectric constant [28]:

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - (\hbar\omega)^2} \quad (9)$$

With E_0 is the average excitation energy; E_d the dispersion energy. They are obtained by plotting $(n^2 - 1)^{-1}$ as a function of $(\hbar\omega)^2$ and a linear fitting is proceed where the slope is $(E_0 E_d)^{-1}$ and the intercept is E_0 / E_d .

The values obtained for E_0 and E_d of the Mn_3O_4 : Sn (0, 2, and 4 at %) thin films are presented in Table 3. Also, the static refractive index, n_0 , and the dielectric constant, ϵ_∞ , are extracted as follow and they are presented in table 3 [29]:

$$n_0 = \sqrt{1 + \frac{E_d}{E_0}} \quad (10)$$

$$n_0 = \sqrt{\epsilon_\infty} \quad (11)$$

The n_0 and ϵ_∞ are decreasing as the doping concentration increases. This decrease can be correlated to the presence of the tensile strain in the lattice. This last increases the interatomic distances, leading to a change in the electronic structure (photoelastic effect). We further investigated the nonlinear optical properties of Mn_3O_4 : Sn (0, 2, and 4 at %) by adopting the Ticha and Tichy model [30] where the linear optical susceptibility χ^1 , the third-order nonlinear optical susceptibility χ^3 and the nonlinear refractive index n_2 are determined as follows [31]:

$$\chi^1 = \frac{E_d E_0}{E_0^2 - (\hbar\omega)^2} \quad (12)$$

$$\text{As the } \hbar\omega \text{ extrapolate to } 0, n=n_0 \text{ thus, } \chi^1 = \frac{n_0^2 - 1}{4\pi} \quad (13)$$

$$\text{Given the miller generalized rule we obtain: } \chi^3 = A (\chi^1)^4 = A \left(\frac{n_0^2 - 1}{4\pi} \right)^4$$

$$n_2 = \frac{12\pi\chi^3}{n_0} \quad (14)$$

All the obtained values are presented in Table 4. Vinges et al. [23] have found a similar values of the χ^3 from $0.074 \cdot 10^{-11}$ (esu) to $61.774 \cdot 10^{-11}$ (esu) as they increased the value of the starting solution from 0.04 M to 0.20 M. The χ^3 values decrease as the tin doping concentration increases (Figure 9). The decrease in χ^3 and n_2 values can be associated with multiple parameters, such as the poor crystallinity of the $Mn_3O_4:Sn$ (2 and 4 at %) thin films [32], where a better crystallinity can lead to a better response in the nonlinear optical parameters; the tensile strain effect that reduces the static refractive index and also decreases the E_g that have a direct relation with the polarization response, where its increase can be translated by a strong polarization; and vice versa [33]. Hence, the understanding of the polarization degree in materials is of significant interest. Hence the decrease in the nonlinear optical properties of tin doped Mn_3O_4 (2 and 4 at %) compared to undoped Mn_3O_4 thin films.

Further, multiple properties of materials such as the linear refractive index [34], optical band gap energy [34] and electronegativity [35] can be implemented to estimate the average electronic oxide polarizability there for the state of polarization. Dimitriv et al. [34] have established a correlation where the decrease of the linear refractive index will decrease the polarizability. The increase of the optical band gap energy will lead to a decrease of the polarizability. Thus, the decrease of polarizability will lead to a decrease of the optical nonlinear susceptibility. Hence, figure (8-c) and figure (9) of the linear refractive index and the third order susceptibility shows similar plots for all thin films as a function of wavelength/frequency.

Table 3: Linear and nonlinear optical parameters of $Mn_3O_4:Sn$ (0, 2, and 4 at %) thin films by Ticha and Tichy approximation.

$Mn_3O_4:Sn$ (x at %)	E_d (eV) $\pm \Delta E_d$	E_0 (eV) $\pm \Delta E_0$	$\chi^1 \pm \Delta \chi^1$	$n_0 \pm \Delta n_0$	ϵ_∞	$n_2 \pm \Delta n_2 \cdot 10^{-11}$	$\chi^3 \pm \Delta \chi^3 \cdot 10^{-13}$ (esu)
0	5.44 ± 0.008	1.77 ± 0.002	0.25 ± 0.009	2.02 ± 0.003	4.08	1.14 ± 0.023	6.14 ± 0.11
2	5.10 ± 0.008	1.96 ± 0.008	0.21 ± 0.014	1.89 ± 0.005	3.57	0.60 ± 0.023	3.00 ± 0.103
4	4.86 ± 0.014	1.97 ± 0.006	0.19 ± 0.015	1.86 ± 0.005	3.45	0.51 ± 0.02	2.50 ± 0.09

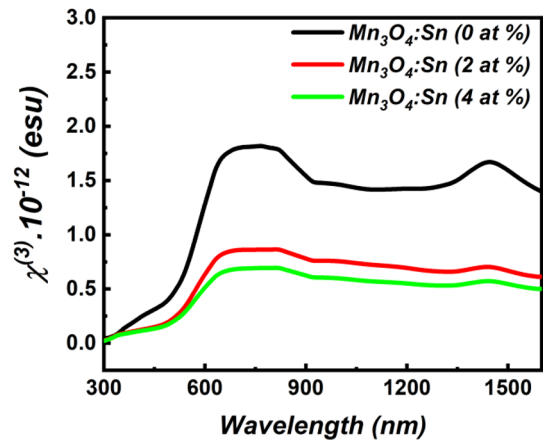


Figure 9: Third order nonlinear susceptibility of Sn doped Mn_3O_4 (0, 2, and 4 at %) thin films by Ticha and Tichy approximation.

4 Conclusion

Undoped and tin doped manganese oxide (0, 2, and 4 at %) thin films were elaborated by spray pyrolysis technique. The physicochemical properties presented in the structural characterization showed a tetragonal crystal structure for all thin films. A surface morphological characterization was carried out with a quantitative analysis of the elements that showed the presence of manganese, oxygen, and tin. Finally, a linear and nonlinear optical study of the thin films shows an increase of transmittance and the bandgap energy with tin concentration and a decrease of the nonlinear part in the third order susceptibility from $6.14 \cdot 10^{-13}$ (esu) to $2.50 \cdot 10^{-13}$ (esu) and in the nonlinear refractive index from $1.14 \cdot 10^{-12}$ to 0.51

10^{-12} . This decrease can be originated from the poor crystallinity, tensile strain, the decrease of polarizability through the decrease of the linear refractive index and the increase of the band gap energy. Hence, the undoped and tin doped manganese oxide (2 and 4 at %) are a good material for nonlinear optical applications

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