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Linear and nonlinear optical discussions of nanostructured Zn-doped CdO thin films

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ABSTRACT

Here, we report the doping effect of zinc (Zn) on the physical properties of cadmium oxide (CdO) at various concentrations (1, 2, 3 and 4 wt% of Zn). The studied samples were prepared using sol-gel in addition with sol gel spin coating technique. The structural, optical and dispersive properties were compared with the already reported work in the literature. The structural properties were observed by using atomic force microscopy (AFM). The AFM images show that the grain size decreases with increasing the concentration of Zn. The highest value of average cluster size (78. 71 nm) was found at 1% and the lowest (60.23 nm) when the doping concentration of Zn was 4%. Similar trend was observed in the roughness of the doped thin film when the Zn concentration was increased. The optical properties were examined using Shimadzu UV–Vis–NIR spectrophotometer and we found that the optical band gap of the un-doped CdO and the Zn-doped CdO thin films increases from 2.54 to 2.62 eV as the Zn concentration is increased from 1% to 4%. Also, the optical dispersion parameters (E_o, E_d, n^2_∞, λ_0 and S_o) were calculated and discussed. We observed that the refractive index dispersion of undoped CdO and the Zn-doped CdO thin films follow the single oscillator model. Finally, spectroscopic method has been exploited to analyze the 3rd order non-linear optical susceptibility $\chi^{(3)}$ and nonlinear refractive index $n^{(2)}$.

1. Introduction

In the recent years, many researchers are interested to study the influence of doping of elements with different concentration on some physical properties of CdO to improve its properties like, Al [1,2], Pt [3], Li [4], B [5], Ga [6–8], Cu [9] and Zn [10–12]. Since the CdO has been considered as an important transparent conducting oxide (TCO) materials and is used in diverse applications like transparent contacts for solar cells, optoelectronics, liquid crystal devices, low-emissivity glass windows, EMI shielding, touch screens and flat panel displays. The developments of the TCOs were reported in late 70's but has in fact been famous for nearly a century. As the CdO was the first TCO and was being used in the solar cells since early 1900's. Due to its large energy band gap, which is almost equal to 2.5 eV [13], CdO is being used in several applications such as in solar cells, photodiodes, phototransistors [14], gas sensor [15], optoelectronic devices [9] and due to high optical transmittance it is being used in the visible part of the solar spectrum [16]. Nowadays, new ideas are being developed for the charge carrier layers in transparent transistors, dye-sensitized solar cells, organic solar cells, and solar cells.

Cadmium oxide has been considered as a suitable II – IV n-type semiconductor material because it has a large transmittance in the UV and visible regions of the electromagnetic spectrum coupled with eminent ohmic conductivity. Here, we report the characterization of doped and undoped CdO thin films prepared by easy and simple sol-gel spin coating technique. Literature review shows that materials such as Al, In, F, Mn were used as dopant materials for the preparation of CdO thin film but, there are very few reports published on Zinc-doped CdO thin films. There are several methods to prepare CdO thin film such as SILAR method [17], spray pyrolysis [18], vacuum evaporation [4], solid-state reaction (SSR) [19], dc magnetron sputtering [20], pulsed laser deposition [21] and sol-gel technique [1]. The sol-gel spin coating method has many characteristics to use for the preparation of CdO such as low coast, simple, relatively safe in the handling the cadmium compounds [22]. Both CdO and ZnO are important materials for the use of window materials in the photovoltaic industry. For example,

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Faizullah published his report on the Al and N doped CdO thin films for optical and electrical properties [23]. Zhou et al. report on CdO-ZnO nano-composites for enhanced detection of CO gas and ethanol sensor [6,7]. Transition metal oxides are thought to be novel nonlinear optical (NLO) materials with high 3rd order non-linear optical susceptibility according to familiar Miller's rule because most of them have a high refractive index. Ando et al. [24] have reported that several transparent metal oxide sol-gel thin films such as V_2O_5, Cr_2O_3, Mn_2O_4, Fe_2O_3, Co_3O_4, CuO, and NiO have a high $\chi^{(3)}$ and fast response time using phase conjugation type degenerate four wave mixing method. So, we applied the sol gel spin coating method to fabricate transparent pure and Zn doped cadmium oxide thin films on glass substrate. According to the best of our knowledge, so far, a description regarding 3rd order nonlinear optical properties has been rarely reported for the un-doped and Zn doped CdO thin films.

In this article, we completed the previous work on CdO [1] by studying the influence of Zn doping on CdO thin films prepared by sol-gel spin coating technique on the structural, optical, dispersion properties, third order nonlinear optical susceptibility and compared with other work reported in the literature.

2. Experimental details

2.1. Synthesis of undoped and Zn-doped CdO nanostructured thin films

CdO thin films were fabricated with the precursors cadmium acetate ($Cd(CH_3COO)_2{\cdot}2H_2O$), 2-methoxyethanol ($C_3H_8O_2$) and mono-ethanolamine (C_2H_7NO) [3]. 0.5 M solution of $Cd(CH_3COO)_2{\cdot}2H_2O$ was first added in $C_3H_8O_2$ and left for two hours at normal 60 °C by using hot plate/magnetic stirrer. After 1 h that C_2H_7NO was introduced to this mixture. The molar ratio of C_2H_7NO to $Cd(CH_3COO)_2{\cdot}2H_2O$ was fixed as 1.0. The cadmium oxide solution was prepared with the different concentration of zinc doping, *i.e.,*1,2, 3 and 4 wt% by using zinc acetate $Zn(CH_3COO)_2{\cdot}2H_2O$. The prepared solution was homogenized through stirring at 60 °C for about 30 min until the clear solution is obtained. The prepared solution was then aged at room temperature for 48 h before the deposition was carried out. The CdO thin films were coated on a glass substrate by sol-gel spin coating technique and after that, the films were left for drying at 150 °C for 10 min by using a hot plate so that it could help to evaporate the solvents. This process is repeated for 10 times to gain the required film thickness of doped and undoped CdO. The un-doped and Zn-doped CdO thin films were heated at 450 °C for 2 h in an electric furnace for annealing and to concert the metal hydroxide to metal oxides and to remove any other organic residuals in the solutions.

2.2. Characterizations

The thicknesses of the fabricated films were measured by atomic force microscope microscopy and equal 180 nm for all thin films. Also, surface morphological studies were performed using a PARK system XE 100E SPM in non-contact mode.

The optical, reflectance, transmittance and absorbance properties of undoped and Zn-doped CdO films were studied using a Shimadzu UV–Vis–NIR 3600 spectrophotometer in the wavelength range of 240–860 nm.

3. Results and discussion

3.1. Surface morphology properties of undoped and Zn-doped CdO nanostructured thin films

The surface morphological analysis for un-doped and Zn-doped CdO thin films was performed by using scanning probe microscopy. Fig. 1(A-E) indicate the AFM images for undoped and Zn-doped CdO films for different concentration of Zn (1, 2, 3 and 4 wt%). The nanoclusters sizes and surface roughness of the undoped and Zn-doped CdO thin films were evaluated and tabled in Table 1. These values show that the grain size of CdO seems to depend upon the Zn doping. As seen from the Table 1, the average cluster size decreases from 78.72 to 60.23 nm when zinc dopant concentration was increased from 1% to 4% and similar trend was observed in the roughness of the film which was reduced from 56.29 to 20.46 nm. The crystalline size may be reduced because of the lattice distortion caused by radii difference between the Zn dopant and the cadmium element. As, oxygen vacancies also play an important role in structure mobility, therefore, we observe smaller crystalline size and also the particle size. The similar result was evident from the study carried out by Z. Serbetci et al. [3] for Pt-doped CdO thin films. This explains the influence of Zn with different concentration which improves the structural properties of CdO thin films by controlling the average cluster size and roughness of the doped films.

3.2. Optical properties of undoped and Zn-doped CdO nanostructured thin films

Figs. 2–4 show that the *T(λ)*, *R(λ)* and, *abs(λ)* spectra of the undoped and Zn-doped CdO films examined in the wavelength from 240 to 860. From Fig. 2, we can observe that in the beginning transmittance increases until wavelength is nearly 550 nm and then becomes independent of the wavelength of the incident light beam. It was also noted that the transmittance decreases when the Zn-doping was increased. From Fig. 2, we can observe that the reflectance of the films increases with wavelength upto 500 nm and then decreases with increasing wavelength. However, it can also be observed that reflectance increases with increasing Zn-doping. The high *T(λ)*, and low *R(λ)* values obtained for the deposited films, make the films suitable as an antireflection coating material for applications in solar cell industry [18]. The absorption coefficient α was calculated from the experimental measurements given by relationship [25–27]:

$$\alpha = \frac{abs}{t}, \tag{1}$$

where t is the thickness of films. To calculate the optical band gap and know the type of transition, we used the Tauc's relationship [28]:

$$\alpha h\upsilon = A(h\upsilon - E_g)^m \tag{2}$$

where α indicates the absorption coefficient, A is taken as constant, h represents the Planck's constant, υ is the frequency of the incident photon and E_g is the optical band gap and the exponent m normally depends upon the transition type, m =1/2, 2, 3/2 and 3 represents to allowed direct, indirect, forbidden direct and forbidden indirect transitions respectively. From the analysis, we found that m=1/2 for CdO and Zn-doped CdO, therefore we may conclude that it exhibits direct transition. From Fig. 5 band gap values were inferred from the linear region of the plot $(\alpha h\upsilon)^2$ versus $h\upsilon$ curves of CdO films with diverse doping percentages of Zn and tabulated in Table 2. The value of optical band gap for undoped CdO equal 2.54 eV and it is in concurrence with other work [2,7,22]. Also, we can see that the optical band gap energy increases with increase in Zn concentration. A similar result was reported by [18,29]. To determine the localized states widths (E_u) called Urbach's energy, we used Pankove's expression [30]:

$$\alpha(h\upsilon) = AE_u^{3/2}\exp(h\upsilon/E_u), \tag{3}$$

where E_u is a parameter that is used to describe the localized state width in the band gap,α shows the absorption coefficient, A is used as a constant, $h\upsilon$ is the photon energy of light. Semi-logarithm plots of α against the photon energy are shown in Fig. 6. The empirical parameter E_u was obtained and tabulated in Table 2. It is shown that the Urbach's energy for the undoped film has the smallest width of the tails and increasing with Zn doping. The increased value of E_u could be noticed

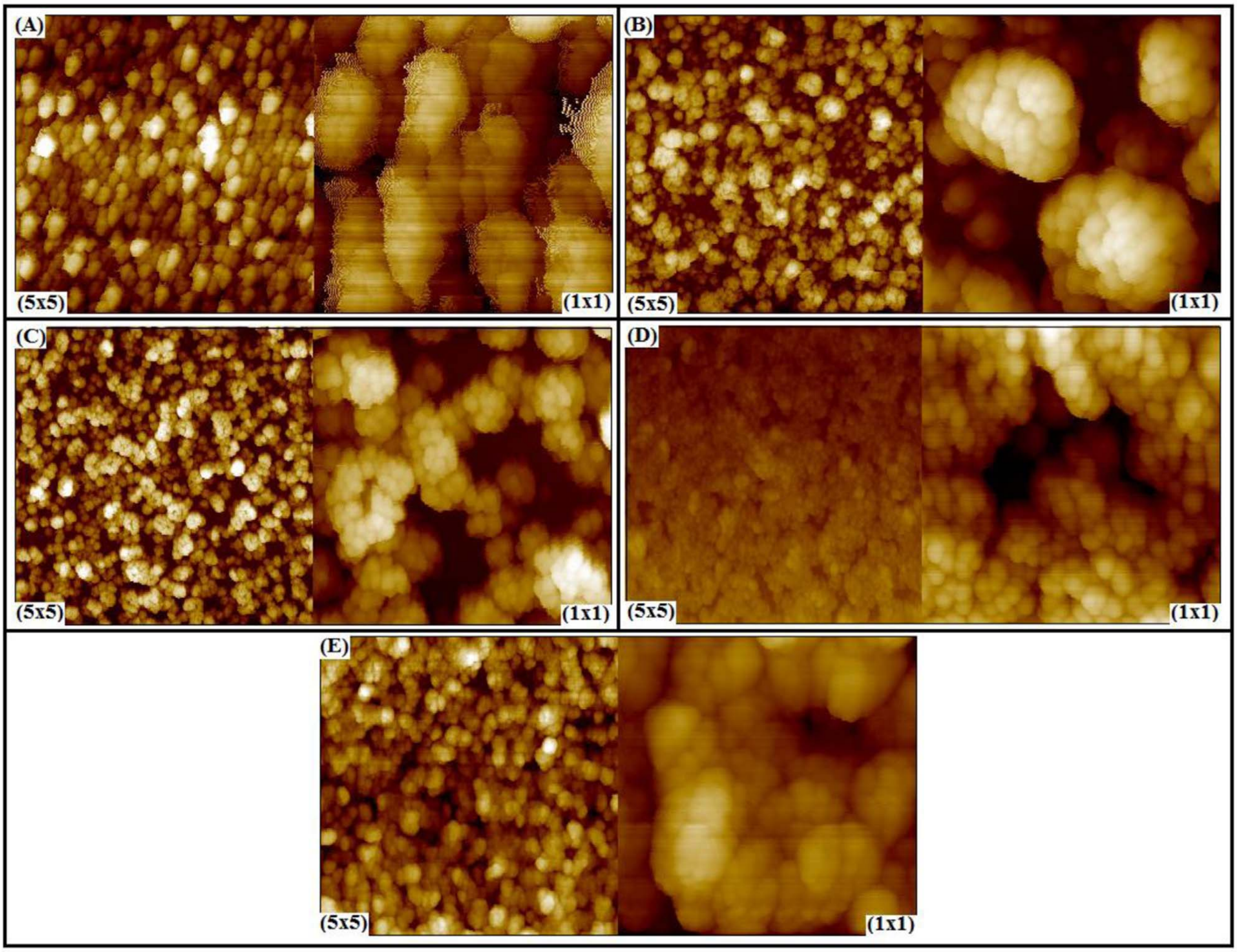

Fig. 1. AFM- 2D images of(5×5 μm^2) and (1×1 μm^2) for (A) undoped CdO, (B) 1 wt%, (C) 2 wt%, (D) 3 wt% and (E) 4 wt% Zn-doped CdO thin films.

Table 1
The calculated average clusters size and the surface roughness for un-doped and Zn doped CdO with different Zn-doped ratios.

Samples	Average clusters size (nm)	Surface roughness (nm)
Undoped CdO	71.68	25.03
1% Zn **doped** CdO	78.71	56.29
2% Zn **doped** CdO	70.03	39.26
3% Zn **doped** CdO	68.34	30.71
4% Zn **doped** CdO	60.23	20.46

because of increased concentration of defects were observed for this sample. A similar result was reported by Usharani and co-workers [18] for Zn-doped CdO thin films and for Al-doped CdO thin films by Yahia et al. [1].

3.3. Optical dispersion properties of undoped and Zn-doped CdO nanostructured thin films

In order to determine optical dispersion parameters (E_o, E_d, n^2_∞,λ_0 and S_0) for undoped and Zn-doped CdO, we should be calculating the n and k which is given by the well-known Fresnel formula as below [31,32]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \tag{4}$$

where n = refractive index, k= absorption index and $k=\alpha\lambda/4\pi$. If one solves Eq. (4) via elementary algebraic manipulation, the refractive index is found by:

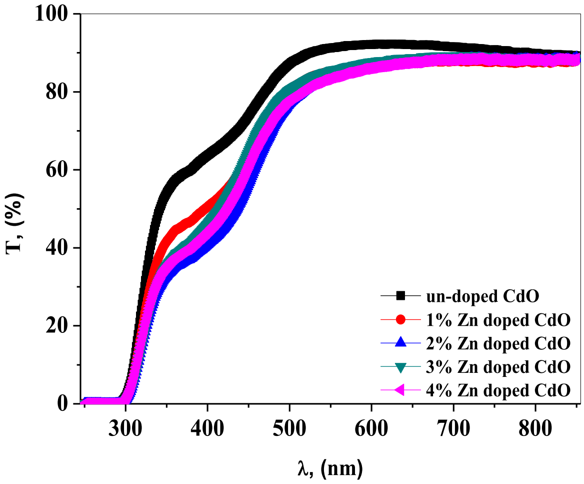

Fig. 2. Transmittance spectra for undoped and Zn-doped CdO thin films.

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2}, \tag{5}$$

Figs. 7 and 8 show the plots of k and n vs λ for the undoped and Zn-doped CdO thin films. From Fig. 8, we can observed that values of n of the Zn-doped CdO films increase with increasing Zn concentration. The

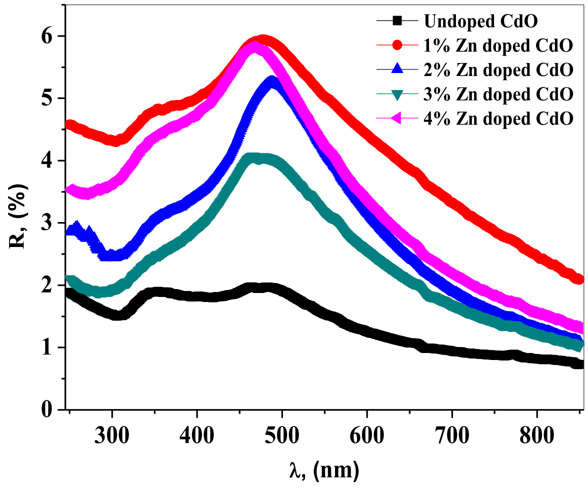

Fig. 3. Reflectance spectra for undoped and Zn-doped CdO thin films.

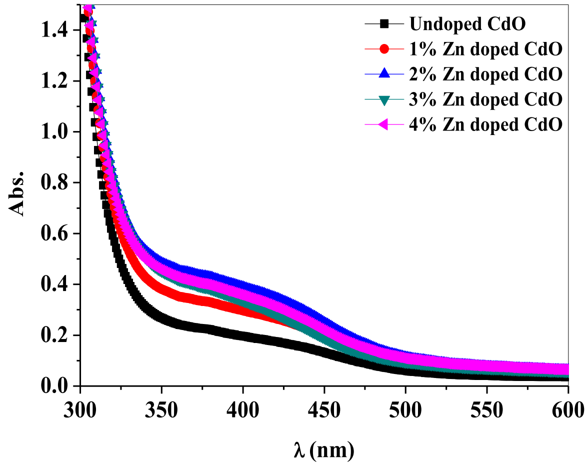

Fig. 4. Absorbance spectra for undoped and Zn-doped CdO thin films.

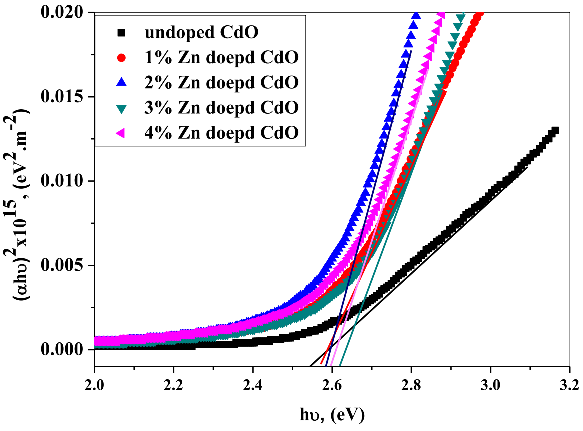

Fig. 5. Plotting of $(\alpha h\nu)^2$ versus $h\nu$ for un-doped and Zn-doped CdO thin films.

plot of n is composed of two regions which are termed as abnormal and normal dispersion [3].

1. Abnormal dispersion region:
   The values of undoped and Zn-doped CdO films increase with the increased value of λ.
2. Normal dispersion region:
   The n values of un-doped and Zn-doped CdO films decrease with the increased wavelength [3,30].

Table 2
Optical band gap and optical dispersion parameters for undoped and Zn doped CdO thin films with different Zn-doped ratios.

Samples	Optical band gap E_g, (eV)	(E_u), (eV)	Dispersion parameters (E_o), (eV)	(E_d), (eV)	$\varepsilon_i = n_\infty^2$	λ$_o$ (nm)	S$_o$ (m)$^{-2}$
Undoped CdO	2.54	0.31	2.81	1.42	1.42	310.75	4.45×10^{12}
1% Zn -doped CdO	2.57	0.36	2.00	2.30	1.90	352.9	7.23×10^{12}
2% Zn -doped CdO	2.59	0.38	2.22	1.95	1.58	359.16	4.46×10^{12}
3% Zn -doped CdO	2.62	0.45	2.30	1.81	1.58	366.2	4.33×10^{12}
4% Zn -doped CdO	2.59	0.50	2.14	1.95	1.66	405.55	4.01×10^{12}

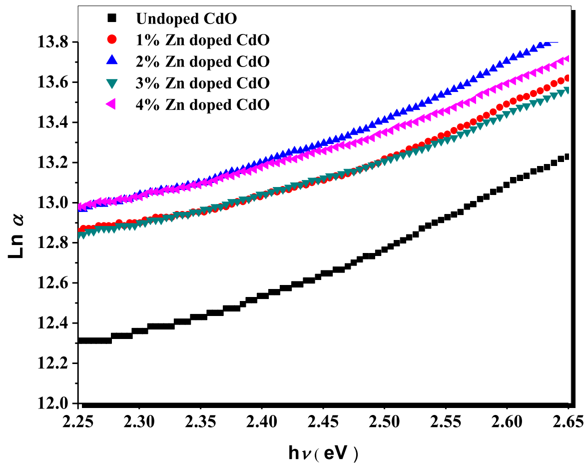

Fig. 6. Plots of ln α versus $h\nu$ for un-doped and Zn-doped CdO thin films.

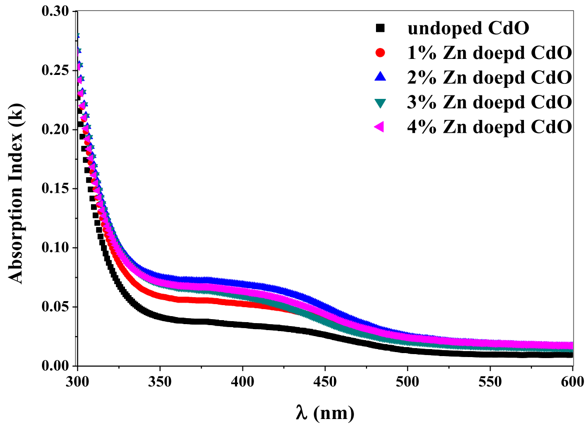

Fig. 7. The dependence of the absorption index, k on the wavelengths for undoped and Zn-doped CdO thin films.

To enquire the n dispersion of the undoped and Zn-doped CdO films, the single oscillator model has been introduced by DiDomenico and Wemple [33]:

$$n^2 - 1 = \frac{E_d E_0}{E_0^2 - (h\nu)^2}, \tag{6}$$

where n indicates the refractive index and E_o denote the single-

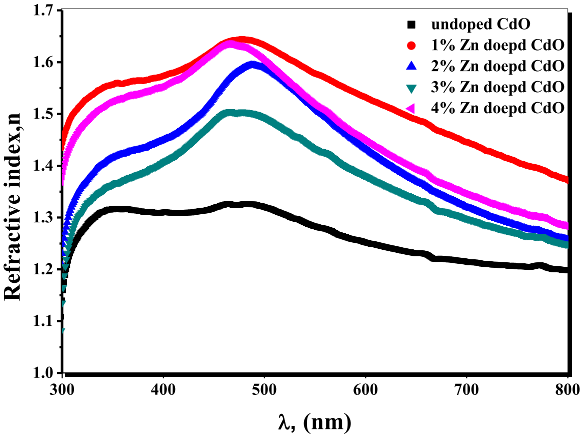

Fig. 8. The dependence of the refractive index n on the wavelengths for undoped and Zn-doped CdO thin films.

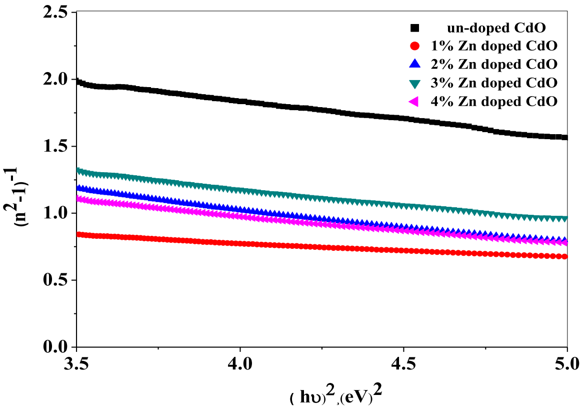

Fig. 9. Plotting of $(n^2{-}1)^{-1}$ versus $(h\upsilon)^2$ for undoped CdO and Zn-doped CdO thin films.

oscillator energy for electronic transitions whereas E_d is indicating the dispersion energy. The dielectric response for transitions is defined below with the optical gap by using this model. Fig. 9 shows that if the Plot of $(n^2{-}1)^{-1}$ vs $(h\upsilon)^2$ is taken into consideration, it would allow us to define the parameters of the oscillator. E_d and E_o values were calculated from the line of the slope and the intercept on the vertical axis. E_o and E_d for undoped and Zn-doped CdO films were determined and tabulated in Table 2. The value of the index of refraction at infinite wavelength n_∞ can be accessed from the following relation [34]:

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_0}{\lambda}\right)^2 \tag{7}$$

and the average oscillator strength S_o can be expressed as below [35]:

$$n^2 - 1 = \frac{S_0\lambda_0^2}{1 - (\lambda_0/\lambda)^2} \tag{8}$$

where λ indicates the wavelength of the incident light whereas the λ_0 denotes the average oscillator wavelength. From Eq. (8) the strength of the average oscillator is usually given by:

$$S_0 = \frac{(n_\infty^2 - 1)}{\lambda_0^2}, \tag{9}$$

The values of $n_\infty^2(\varepsilon_l)$, λ_o and S_o for un-doped and Zn-doped CdO films were established from the slope and intercept in Fig. 10 which showed that the plot of $(n^2{-}1)^{-1}$ vs λ^{-2} and tabulated in Table 2. Nearly the similar result was evident from the study carried out by Serbetci et al. [3] for Pt-doped CdO films.

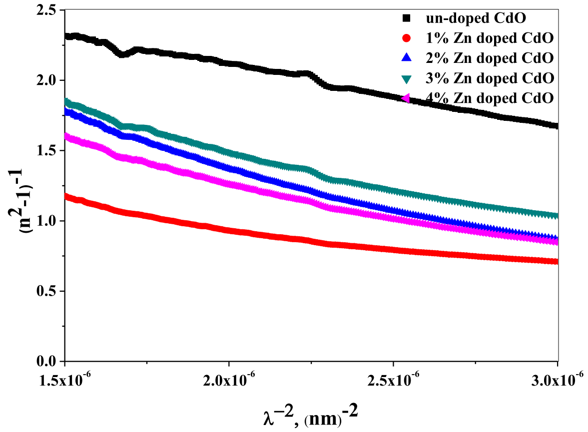

Fig. 10. Plotting of $(n^2{-}1)^{-1}$ versus $(\lambda)^{-2}$ for undoped and Zn-doped CdO thin films.

3.4. Nonlinear optical properties of undoped and Zn-doped CdO nanostructured thin films

Nonlinear optics study has a key role in fundamental applications of all optical signals processing units, optical circuits and switching devices. When a high intensity light transmits through a medium, it generates nonlinear effects. The nonlinear refractive index, n_2 mainly depends upon the intensity of incident light. When the deposited film is exposed to incident light of intense electric field, the polarization and the electric field are no longer in proportion, and the variation in polarizability has to be elongated by the terms which are proportional to the squared electric field [36]. Nonlinear media, that is, the media in which the dielectric polarization, P shows nonlinear behavior with the electric field E, of the incident light, thus the non-linear electron polarizability P_{NL} can be shown by the following equation [37,38]:

$$p = \chi^{(1)}E + P_{NL}, \tag{10}$$

where

$$P_{NL} = \chi^{(2)}E^2 + \chi^{(3)}E^3, \tag{10a}$$

where is the polarizability, $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ are the linear, second order nonlinear and the third order nonlinear optical susceptibility respectively. For $n(\lambda)$ the following expression could be used:

$$n(\lambda) = n_o(\lambda) + n_2(E^2), \tag{11}$$

In the above relation, the refractive index, $n(\lambda)$ follows rule: $n_o(\lambda) >> n_2(\lambda)$ i.e., $n(\lambda)=n_o(\lambda)$ and (E^2) shows the mean squared electric field. The linear optical susceptibility, $\chi^{(1)}$ of a medium can be written by the following equation [39]:

$$\chi^{(1)} = \frac{(n^2{-}1)}{4\pi}, \tag{12}$$

On the basis of $n_o(\lambda)$, the relation between third order nonlinear optical susceptibility, $\chi^{(3)}$ and linear optical susceptibility, $\chi^{(1)}$ according to Millers's generalized rule is shown as [40]:

$$\chi^{(3)} = A(\chi^{(1)})^4, \tag{13}$$

From Eq. (11) and Eq. (12), we can obtain the following relation [41]:

$$\chi^{(3)} = \frac{A}{(4\pi)^4}(n^2{-}1)^4, \tag{14}$$

where $A \approx 1.7\times10^{-10}$ esu, is a quantity that is independent of frequency and mostly it is the same for all materials [42]. Tichy and Ticha relation gives a combination of the Miller's generalized rule and n_o obtained from WDD model which can be explained from the following relation [41]:

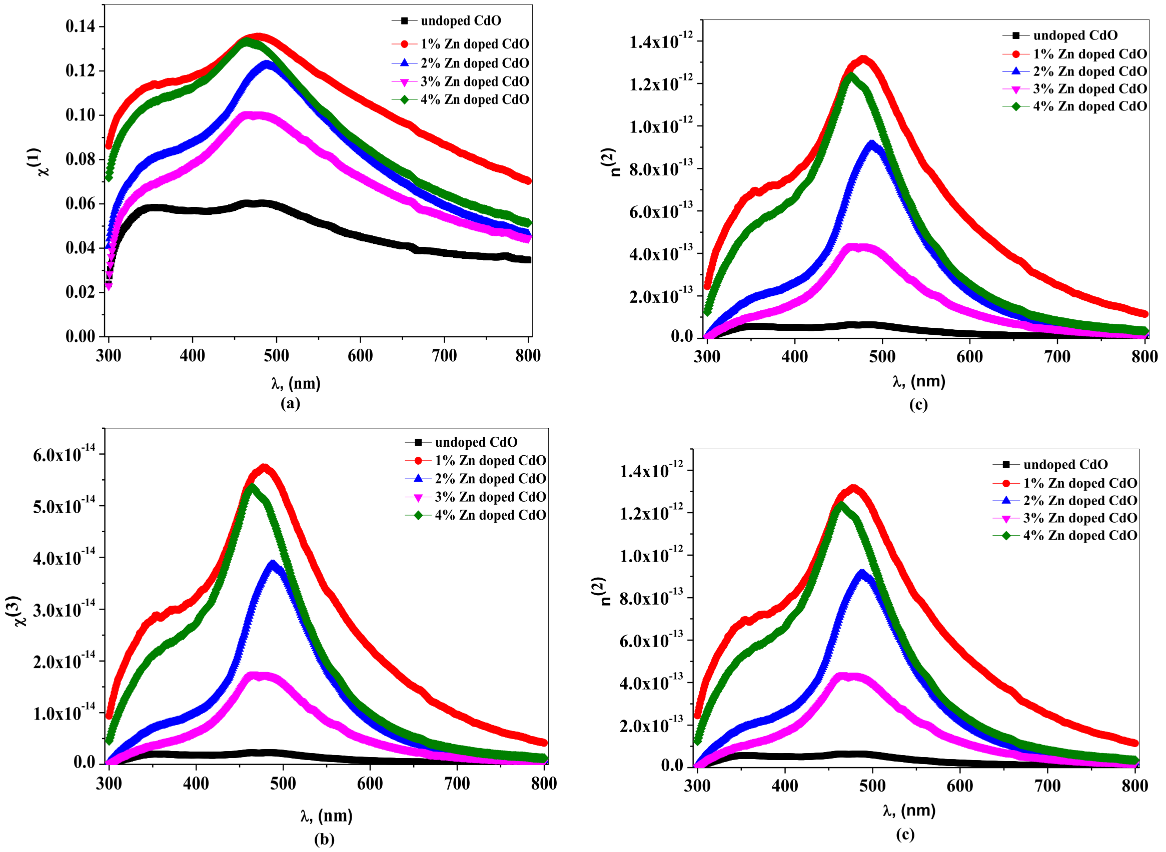

Fig. 11. **(a)**: Plot of linear susceptibility, $\chi^{(1)}$ versus wavelength, λ for undoped and Zn-doped CdO thin film. **(b)**: Plot of third order nonlinear susceptibility, $\chi^{(3)}$ versus wavelength, λ for undoped and Zn-doped CdO thin film. **(c)**: Plot of nonlinear refractive index, n_2 versus wavelength, λ for undoped and Zn-doped CdO thin film.

$$n^{(2)} = \frac{12\pi\chi^{(3)}}{n_0}, \tag{15}$$

Fig. 11(a and b) represents the optical susceptibility, $n^{(2)}$ and 3rd order non-linear optical susceptibility, $\chi^{(3)}$. The results of nonlinear refractive index, n_2 optical susceptibility, $\chi^{(1)}$ and third order nonlinear optical susceptibility, $\chi^{(3)}$ as function of wavelength, λ of incident light are presented in Fig. 11(a- c) for pure and Zn-doped CdO thin films. It can be observed that the incorporation of the zinc doping improves the non linear response. Zinc in much small quantity got incorporated in the CdO lattice and agglomerated on the crystallite and the boundaries of the grains of the host CdO in the amorphous state form [14]. Normally, the doping of Zn in CdO thin films contributes for the replacement of host Cd^{2+} ions with that of Zn^{2+} ions in the host CdO lattice. The doped samples showed the higher values than the undoped. Zinc is believed to cause an increase of nonlinearity within the crystalline Zn-doped CdO films. The highest 3rd order nonlinear value $\chi^{(3)}$ =5.73×10^{-14} (esu) was found for the Zn:CdO when the concentration of Zn is 1% in the sample and the corresponding nonlinear refractive index value, n_2 =1.32×10^{-12} (esu). Our calculated value for third order nonlinear susceptibility is comparable with the reported value for Ce doped ZnO thin films by Sofiani et al. [43]. This may be described by the surface roughness and the better crystallinity of the films. The results show that this materials exhibit large third order nonlinear susceptibility which makes it potentially useful as NLO materials.

4. Conclusion

We presented in this article the influence of Zn-doped CdO prepared by sol-gel spin coating technique on the structural, optical, dispersion and the third order nonlinear optical susceptibility properties follow.

1. The grain size of CdO increases with increasing the concentration of Zn doping.
2. The type of transition for un-doped and Zn-doped CdO films are direct band gap semiconductors and the optical band gap energy increases with increasing Zn concentration.
3. The Urbach's energy for the undoped thin film has the smallest width of the tails and increases with Zn doping. The increased value of E_u observed could be attributed to the increase in the concentration of defects observed for the sample.
4. The dispersion parameters E_o, E_d, $n^2_\infty(\varepsilon_i)$, λ_o and S_0 for un-doped and Zn-doped CdO films were determined and explain that the effect of Zn-doped CdO on these values.
5. The 3rd order nonlinear optical susceptibility value increases remarkably for the Zn-doped CdO when the Zn concentration is 1% compared to un-doped CdO which makes it a suitable material for potential application as NLO.

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