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Effect of Red Laser Irradiation on The Optical Properties of Cobalt oxide (CoO_2) Thin Films deposited via Semi-Computerized Spraying Technique

Bahaa T. Chiad[1], Mushtaq T. Al-Helaly[1,2], Mohammed Sh. Essa[3], Nathera A .Al-Tememee[1]
mushtaq.alhelaly@qu.edu.iq

[1]Department of Physics, College of Sciences, University of Baghdad, Iraq
[2]Department of Physics, College of Education, University of Al-Qadisiyah, Iraq.
3Renewable Energy Directorate, Ministry of Science and Technology Baghdad, Iraq

Abstract. The existing investigation explains the consequence of irradiation of red laser on the optic properties of (CoO_2) films. The film was equipped by the utilization of semi-computerized spray pyrolysis technique (SCSPT), it is the first time that this technique is used in the preparation and irradiation using a laser in this technique. From the XRD analysis, the crystalline existence with trigonal crystal system was when the received films were processed by continuous red laser (700 nm) with power (>1000mW)for different laser irradiation time using different number of times a laser scan (0, 6, 9, 12, 15 and 18 times) with total irradiation time(0,30,45,60,75,90 min) respectively at room temperature. The optic properties of CoO_2 thin samples was struck by light of red laser. The parameters such as the absorbance, coefficient of absorption coefficient of extinction refractive index, optic conductivity, the realε_1 and imaginaryε_2part of the dielectric constant of the films rises subsequently by laser irradiation, only the transmittance was decremented with laser ray of light. The optic energy gap was reduced from (1.91eV) without irradiation to (1.57eV) and subsequent laser irradiation, and there is a great alteration of optical energy gap values for photovoltaic (PV) utilization. As the results showed that the laser irradiation method has a clear change in the optical properties with less time and energy than the traditional annealing methods, this is the aim of the study.

Key words red laser irradiation, semi-computerized spray system, CoO_2, optic properties.

1.Introduction

Spray pyrolysis method (SPT) is quite possibly the almost encouraging procedures utilized to get the metal oxide thin films like CoO_2, ZnO, CuO, and CeO_2, and so forth [1,[2]. The SPT procedure accomplishes the necessary similarity for the advancement of sun based cells, P-N intersection diode, hetero intersection diodes, and electrochemical terminals [3].

SPT is almost widely recognized nowadays due to its relevance to delivering an assortment of directing and semiconductor materials. Spraying technique is a striking technique for integrating slight region that used for various applications. Spraying technique has a few highlights, for example, cheapness, no vacancy chamber needed, and the capacity to integrate thin films [4]. On account of films, it tends to be showered over a region bigger than a lab-scale that can be utilized at mechanical creation measures [5]. Five species of cobalt oxide (CoO_2, Co_2O_3, CoO(OH),Co_3O_4, and CoO) Cobalt oxide thin films have attracted substantial research effort in recent years because their potential application in various technological areas. They can be used as high temperature solar selective absorbers [6].

The warm handling of metallic oxide thin films and Nano based structures is led in a chamber in the heating at high temperatures, contingent upon the checking framework [7].While the deposition is going on, this strategy has numerous issues, for example, extreme warmth, long handling time, and a serious level of loss of energy. Likewise, losses in the power are utilized for expanding and diminishing the surface temperature and the actual heater. In add-on this, this cycle is contrary with thermic delicate substratum, where the exorbitant temperatures can modify the micro functional modification and expansion of heat mismatch, primary to mechanical disappointments. Besides, thermal systems dependent on customary heating strategies can't initiate spatially settled warm impacts, involving the Nano structures to be actually isolated from the advanced hardware. The issuance extent the immediate combination of steel oxide films or Nano structures into the corresponding manufacture cycle of metal oxide semiconductors [8]. The laser illumination measure turned into answers for the preceding issuance and permits instead of all around coordinated metal oxide films and nanostructures. This strategy is particularly founded on the warm impact. That brought about by the laser could keep the temperature discipline at the ideal part with no loss of unreasonable energy [9].Various boundaries could be confronted, for example, laser power, spot width, and checking rate. These boundaries can be differed under dominant for arriving at the ideal warm impact. This framework is described by a fast radically for limited warm impacts that permitting specific oversee the material properties. The warming cycle charges light of laser offer an extent more prominent than the costs of the tempering, which gives a capacity to quick manufacture of materials with negligible force misfortunes. The laser-initiated warm heartedness can be limited to a novel territory in to each one in-plane and dimension bearings. This is plausible to specifically temper the films by thermic hindrance on the basic constructions. Besides, the utilizing of lasers with adequate effectiveness can bring about a sizable decrease in energy needed for warm handling. Relies upon the meaning of the optic proportion to yield laser and the electric force [10].

2. Material and Method

CoO_2 thin films are prepared using the SP technique by mixing raw material as shown in the Table1 in (100) ml of deionized water. Figure1 shows a solution of CoO_2.

Table1: Properties of selective raw materials

Compound	Chemical formula	Molecular weight (gm/mol)	Concentration	Purity	Supplier
Cobalt chloride hexahydrate	$CoCl_2.6H_2O$	273.93088	(0.02) M	98%	Sigma-Aldrich

Figure 1. solution of CoO_2

The CoO_2 films were deposited on the substrate from glass, the substrate temperature was (350±5Co), by using the air as a carrier for precursor solution. The separator between sprayer nozzle and substrate was (35cm) Evaporation and decomposition occurred during the deposition process. The formation reaction of (CoO_2) thin film can be described by the chemical equation below:

$$2\,CoCl_2.6H_2O + O_2 \xrightarrow{Heat} 2CoO_2 \ + 4\,HCl \ + \ 10\,H_2O$$

It is completed by the exploitation of (SCSPT) that was handmade precisely for this product to make and radiation by laser to thin films. For the preparation and irradiation process, this technique is used in the first time. Where in (SCSPT) system the spray nozzle and the irradiation laser move in the plane X-Y according to coordinates such as speed, distance and area of deposition are controlled by the researcher in addition to many other parameters, then studies the optic properties of CoO_2 films before laser irradiation.
Then the CoO_2 films were irradiated at room temperature using the red laser (700 nm) with power (>1000mW) for different time where it was as follows.

Table2. The samples with different time irradiation by violet laser

Sample code	The number of times a laser scan	Total laser irradiation time In minute
X_0	Without irradiation	Without irradiation
X_1	6	30
X_2	9	45
X_3	12	60
X_4	15	75
X_5	18	90

Whereas, for each laser irradiation time takes five minutes along the adult sample (2.5cm) with speed of laser scan (10 mm/min), the length of the laser scanning line was (1.5cm) with a separation between the source and the sample(1cm). The samples were of thickness (1µm) measured in a method interference fringes, and then its optic properties were studied using UV-VIS(K-MAC UV-Vis spectrophotometer (model SV2100, Korea Material & analysis, Korea) after irradiation.

3. Result and Dissection

3.1. XRD of CoO_2

The XRD diagram of the CoO_2 thin films representing a polycrystalline structure. Which shows diffraction peaks at 2 Theta = 31.8306, 24.2525, and 23.4541 with trigonal crystal system. Cell parameters are a= 2.82080 Å c= 4.24030 Å. These values were matched JCPDS 42-1467 Data Card [11].

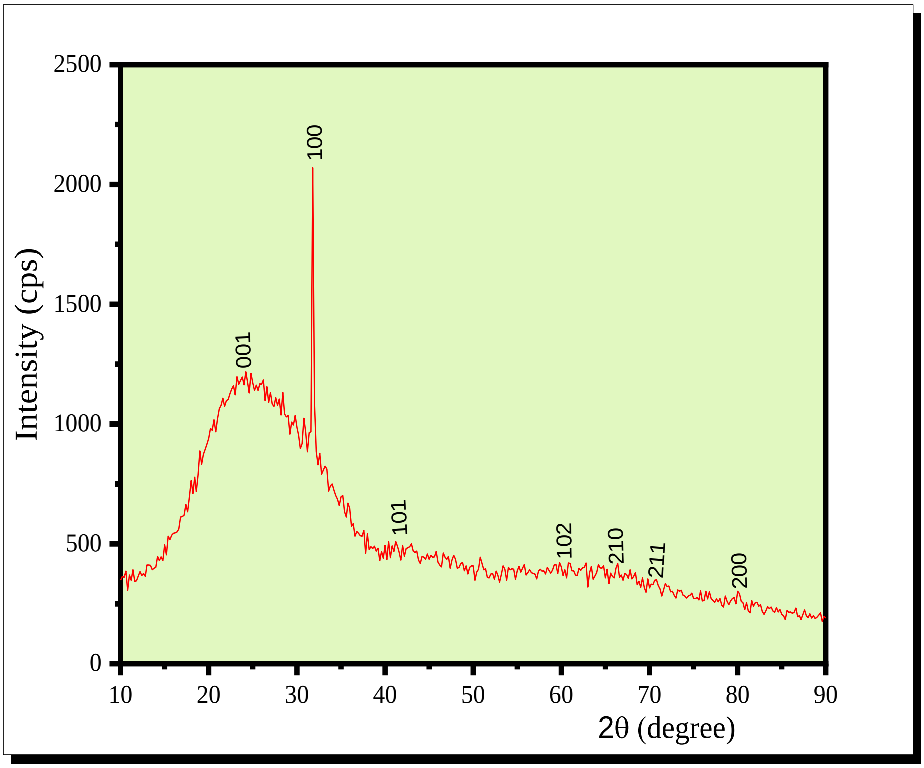


Figure 2. X-ray diffraction diagrams of the CoO_2 thin films

3.2. The Optic Spectrum of CoO_2 Films

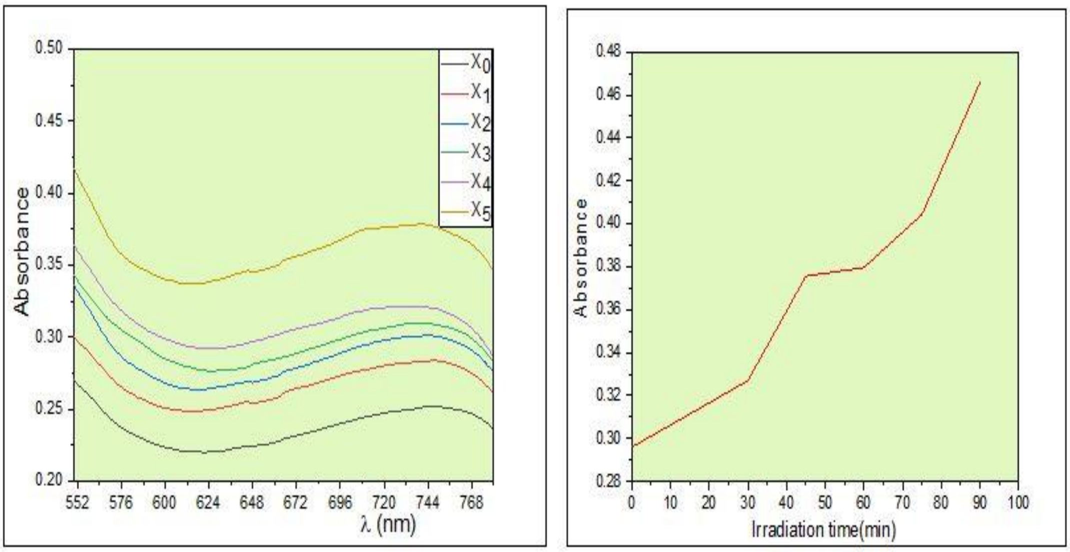
3.2.1. Absorbance

Figure 3.A" demonstrates the optic absorbance (A) of CoO_2 thin films earlier and subsequent ray of red laser in diverse time of laser irradiation. Additional observance displays that the absorbance of the CoO_2 samples will rise afterwards the irradiation of laser as in the table(3) which shows the absorbance change with increasing irradiation time at the wavelength 530(nm), which signifies the middle of the visible range.

Table3. Absorbance at 530(nm) with Irradiation time

Irradiation time(min)	Absorbance at 530(nm)
0	0.296
30	0.327
45	0.37567
60	0.37967
75	0.40433
90	0.46567

This is perhaps credited to change in the grain sizes. The retention edges of the CoO_2 thin films have moved with expanding the laser light time. Two potential components confirm the move of the retention edge. One of that is to amplify of crystallized size that causes the shift in absorption area and the laser employed like tempering temperature to intensify the crystallizing of thin films, this result is an conform with [12,13,14]



A B

Figure 3.A: shows the optic absorbance of CoO_2 films irradiated using red laser in different time.
Figure 3.B: show change of the optic absorbance with the irradiation time at the wavelength 530(nm)

3.2.2. Coefficient of Absorption

The coefficient of absorption is premeditated in the central absorption area using Lambert law [15].

$$I = I_{\circ}\ exp(-\alpha t) \qquad (1)$$

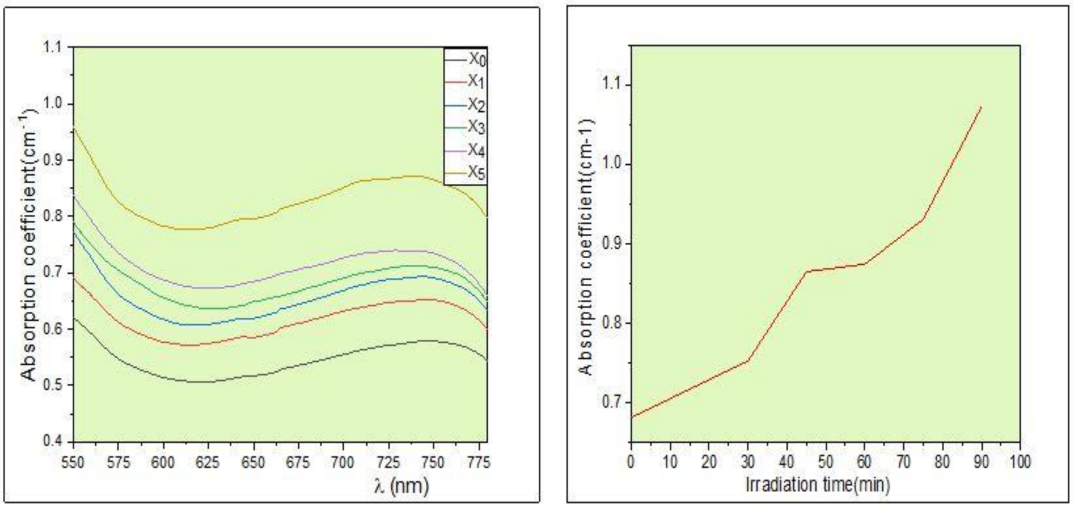
Where t: is film thickness, I: is the intensity of transmitted light. If (I / I_o) = T then:

$$\alpha = 2.303\left(\frac{A}{t}\right) \qquad (2)$$

Figure4. A" demonstrates the coefficient of absorption (α) with wavelength for CoO_2Thin films. The quantity of coefficient of absorption are in range of 10^3 cm $^{-1}$. The detected coefficient of absorbance rises with increasing the irradiation time of red laser which is in conform with earlier reports [14,16].Table(4) proves the variation of the coefficient of absorption with the irradiation time at the wavelength of 530(nm).

Table4. Absorption coefficient with the irradiation time

Irradiation time(min)	Absorption coefficient(cm^{-1}) at 350(nm)
0	0.68169
30	0.75308
45	0.86516
60	0.87437
75	0.93118
90	1.07243



A B

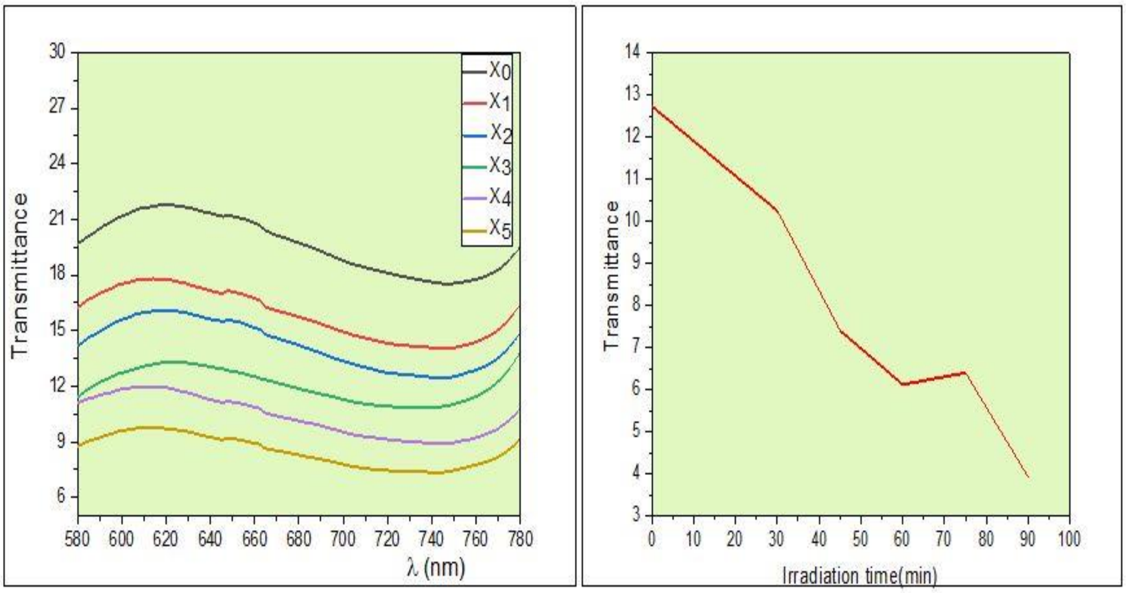
Figure 4.A: Coefficient of absorption of CoO_2 films irradiated using red laser in different time
Figure 4.B: change of the coefficient of absorption with the irradiation time at the wavelength 530(nm)

3.2.3. Transmittance

Figure 5.A" displays the spectrum of transmittance in the range of wavelength (550- 780) nm for the CoO_2 thin films earlier and subsequent irradiation of red laser, which is declined with growing time of irradiation of laser .This outcome is also in pact with earlier reports as absorbance [14,16]. Table 5 it illustrates the change of the transmittance with the irradiation time at the wavelength 530(nm).

Table5. Transmittance with the irradiation time

Irradiation time(min)	Transmittance at 530(nm)
0	12.73
30	10.246
45	7.403
60	6.121
75	6.401
90	3.93



A B

Figure 5.A: Transmittance spectrum of CoO_2 films irradiated using red laser in different time.
Figure 5.B: . Show change of the transmittance with the irradiation time at the wavelength 530(nm).

3.2.4. Index of Refractive

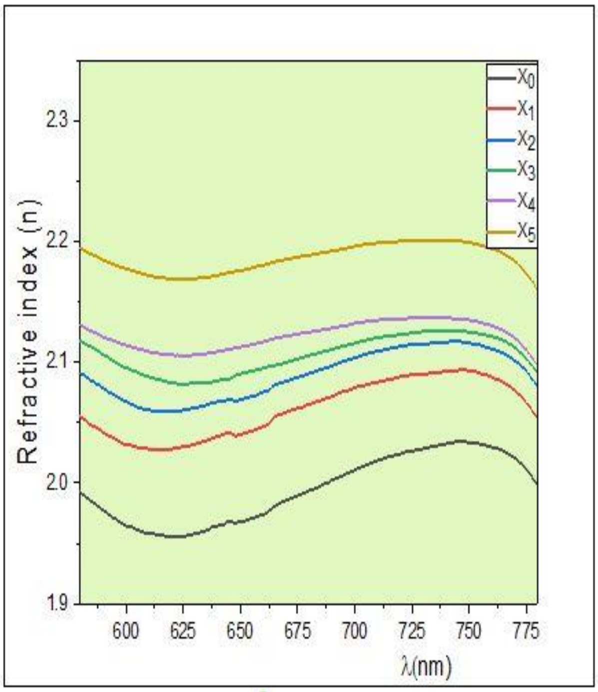
Index of refractive (n) is the primary essential property which can be quantified from the relation [17]:

$$n = \left[\frac{(1+R)^2}{(1-R)^2} - \left(k_\circ{}^2 + 1\right)\right]^{\frac{1}{2}} + \frac{(1+R)}{(1-R)} \qquad (3)$$

Fig.6.A" displays the index of refractive of the CoO_2 sample treated by red laser. The index of refractive of the sample fluctuated between (1.95) earlier and (2.19) subsequent irradiation. It is renowned that the index of refractive rises with increasing the time of irradiation on the CoO_2 thin films. This is owing to the main involvement of electric transition of subsequent laser treatment and this may lead to a momentous variation in the optical parameter [12] [18]. Table (6) shows the variation of the refractive index with the time of irradiation at the wavelength 530(nm).

Table 6. Index of refractive with the irradiation time

Irradiation time(min)	Refractive index at 530(nm)
0	1.30096
30	2.11079
45	2.14086
60	2.15081
75	2.17971
90	2.19685



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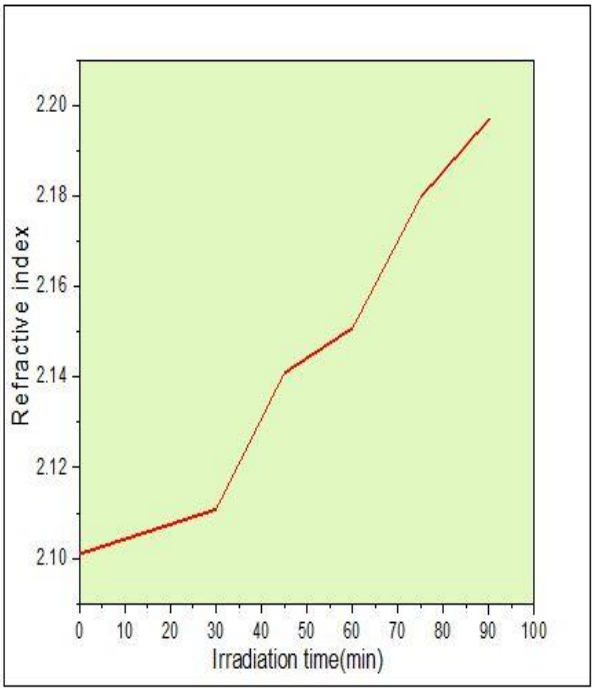


B

Figure 6.A: Index of refractive of CoO_2 irradiated using red laser in different time
Figure 6.B: . change of the index of refractive with the irradiation time at the wavelength530(nm).

3.2.5. Coefficient of Extinction

The coefficient of extinction (K_o) can be assessed by the following [19]:

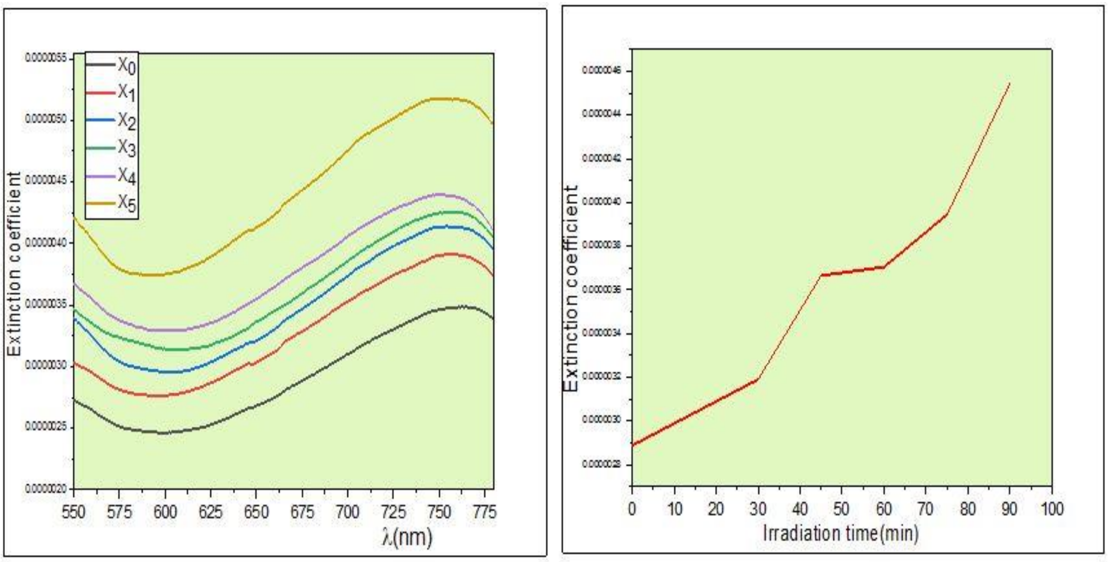
$$K_{\circ} = \alpha \lambda / 4\pi \qquad (4)$$

Where λ: is wavelength and α : The coefficient of absorption

Fig.7.A" displays the distinction of coefficient of extinction with the wavelength earlier and subsequent of red laser irradiation in diverse time. It is well-known that the coefficient of extinction rises with increasing the time of irradiation on the CoO_2thin films which is owing to the increase of coefficient of absorption (α). The outcome is in conform with the earlier reports [14,13]. Table(7) it illustrates the change of the extinction coefficient with the irradiation time at the wavelength 530(nm).

Table 7. Coefficient of extinction with the irradiation time

Irradiation time(min)	Extinction coefficient at 530(nm)
0	2.88763E-6
30	3.19005E-6
45	3.66482E-6
60	3.70384E-6
75	3.94448E-6
90	4.54282E-6



A B

Figure 7.A: Coefficient of extinction of CoO_2 thin films irradiated using red laser in different time**.**
Figure 7.B: change of the coefficient of extinction with the irradiation time at the wavelength 530(nm)

3.2.6 Dielectric constant:

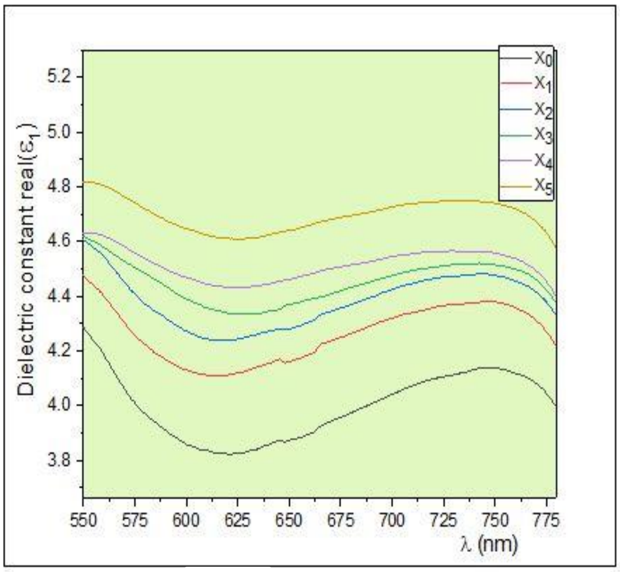
The real (ε_1) and imaginary (ε_2) dielectric constant is measured using the equation [20]:

$$\varepsilon_1 = \left(n^2 - K_\circ{}^2\right) \qquad (5)$$
$$\varepsilon_2 = (2nK_\circ) \qquad (6)$$

Fig.8.A " shows the change with a wavelength in (nm) of the real ε_1 and imaginary ε_2 part of dielectric constant values irradiated using red laser in different time on the CoO_2 films. The real $\varepsilon_1$and imaginary ε_2 part values increase obviously after laser irradiation. This increase is due the ε_1 and $\varepsilon_2$part of dielectric constant dependence of index of refractive (n) and coefficient of extinction (k) the values of which increase with increasing time of irradiation, this result is the conform with [14,16]. Table (8) it illustrates the change of (ε_1) and (ε_2) dielectric constant with the irradiation time at the wavelength 530(nm).

Table 8. Dielectric constant with the irradiation time

Irradiation time(min)	real (ε_1) at 530(nm)	imaginary (ε_2) at 530(nm)
0	4.45545	1.21904E-5
30	4.58329	1.36589E-5
45	4.62599	1.57647E-5
60	4.67124	1.59244E-5
75	4.69611	1.68575E-5
90	4.74875	1.87538E-5



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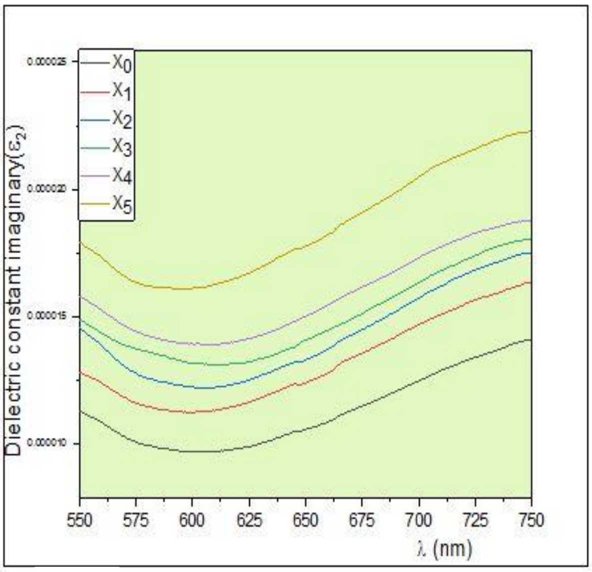
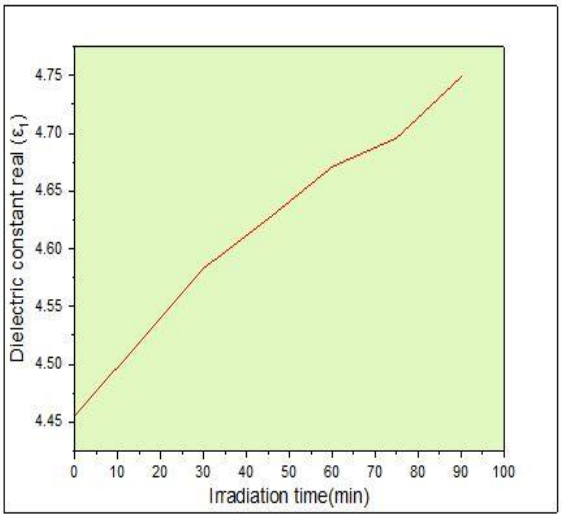
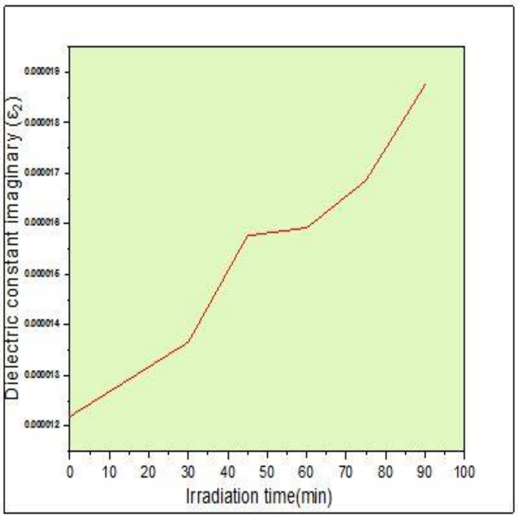


A2

Figure 8.A1: the real part ε_1 of the dielectric constant of CoO_2 films irradiated using red laser in different time

Figure 8.A2: imaginary part $\varepsilon_2$of the dielectric constant of CoO_2 thin films before and after irradiation of red laser in different time





B1 B2

Figure 8.B1: change of the real (ε_1) and imaginary (ε_2) dielectric constant with the irradiation time at the wavelength530(nm)
Figure 8.B2: change of the real (ε_1) and imaginary (ε_2) dielectric constant with the irradiation time at the wavelength530(nm)

3.2.7. Optical Conductivity

Optical conductivity (σ) is expressed in the following relationship[21]:

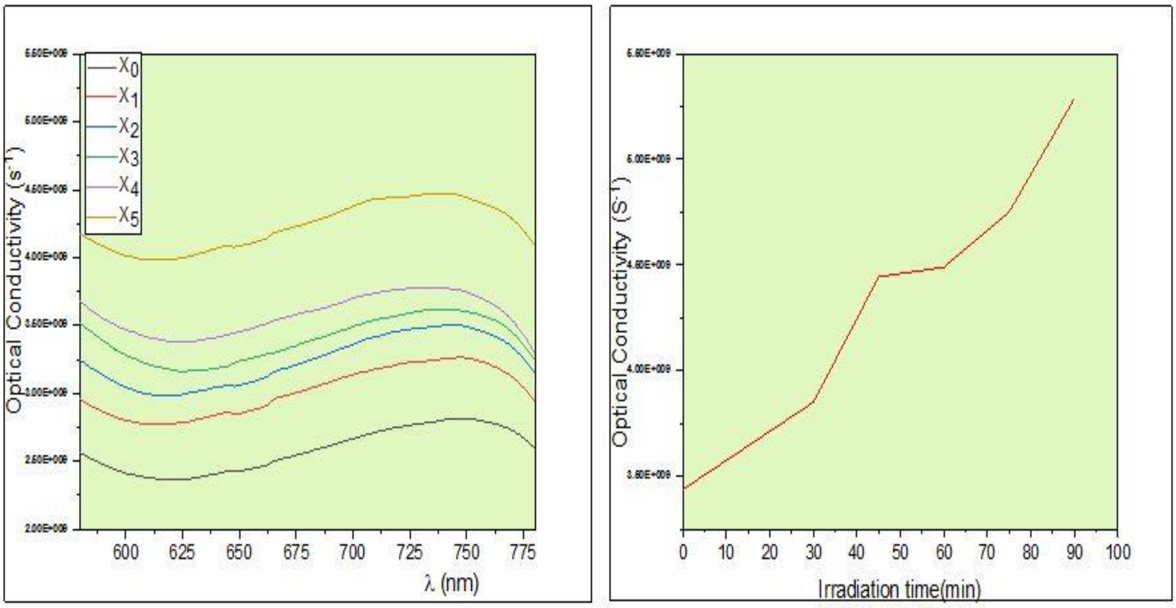
$$\sigma = \frac{\alpha n c}{4\pi} \qquad (7)$$

where c: speed of light.

Fig.9.A" displays the optic conductivity (σ) of CoO_2 films variation of with the wavelength earlier and subsequent irradiation by red laser in diverse time. It is well-known that the optic conductivity increases with increasing irradiation time on the CoO_2 films this is owing to the rise in coefficient of absorption (α) and index of refractive (n). Table(9) illustrates the change of the refractive index with the treatment time at the wavelength 530(nm).

Table 9. optical conductivity with the irradiation time

Irradiation time(min)	Optical Conductivity at 530(nm)
0	3.43687E9
30	3.8509E9
45	4.44458E9
60	4.4896E9
75	4.75268E9
90	5.28731E9



A B

Figure 9.A: optical conductivity of CoO_2 thin films irradiated using red laser in different time
Figure 9.B: change of the optical conductivity with the irradiation time at the wavelength 530(nm).

3.2.8: Optical energy gap
To calculate the optic band gap(E_{opt}) for the thin films, we practice the Tauc's relation as precedes [10]:

$$\alpha\, h\, v = A(hv - E_g)^n \qquad (8)$$

Where A: is constant, hv: energy of photon, Eg :the optic energy gap, and (n) might yield diverse values conferring to the kind transition of electronic.

The (E_{opt}) of CoO_2films earlier and subsequent irradiation by laser have been shown via the relation (4) for indirect (E_{opt}) was proven in "Fig.10". The optical energy gap is lessened from (1.91eV) without irradiation to (1.57eV) after red laser irradiation in different time of CoO_2 films as shown in the table (10) below. The alteration of optic electricity can be well-distinct in expressions of quantum-size influence in which the film with big crystal, so that the resultant in increase in crystalline of CoO_2films and so the density of restricted states lessens ,and this consequence is an conform with previous reports[14,16,22,23].

Table 10. the optical energy gap of samples with different time irradiation by red laser

Irradiation time(min)	optical energy gap(eV)
0	1.91
30	1.85
45	1.7
60	1.6
75	1.65
90	1.57

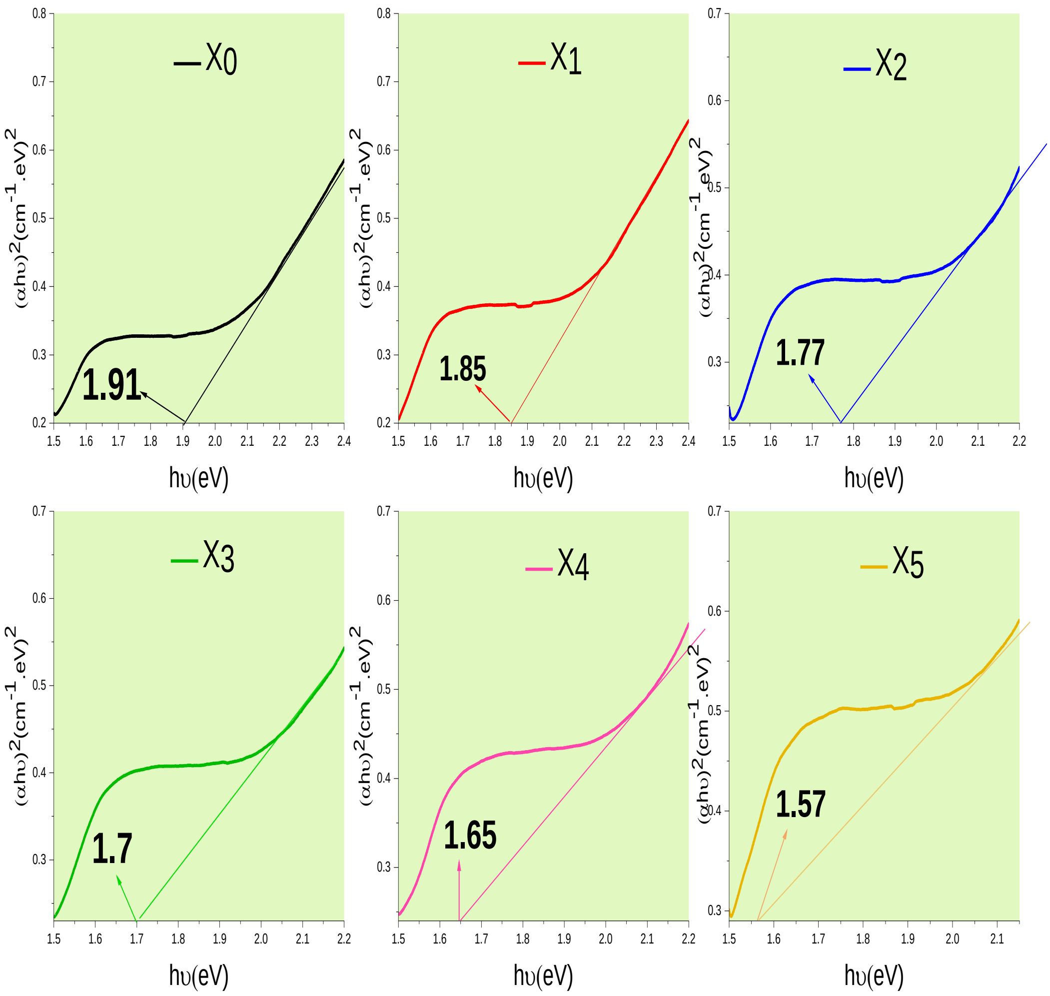


Figure 10.: (Eopt) of CoO2 thin films irradiated using red laser in different time

Conclusions:

The results showed that the method of irradiation with the red laser using the (SCSP) technique is a good to improve the optical properties of CoO_2 thin films commensurate with the applications of renewable energies with less time and energy than the traditional methods , where laser irradiation worked like annealing temperature on the surface of thin films under better conditions than thermal annealing for the researcher to enhance the crystallization of thin films deposited. this is the aim of the study.

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