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STRUCTURAL AND OPTICAL PROPERTIES OF COPPER- DOPED COBALT OXIDE THIN FILMS PREPARED BY SPRAY PYROLYSIS

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ABSTRACT
Copper-doped cobalt oxide ($Cu:Co_3O_4$) films have been prepared by spray pyrolysis (SP) method onto glass substrate at (350) °C with different copper doping concentrations (0%, 1%, 3%, 5%, 7%, 9%) M. Structural and optical properties of the films were studied by X-ray diffraction (XRD) and ultraviolet (UV-Visible) transmission spectra. The X-ray diffraction results revealed that the films consist of Co_3O_4 phase with perfect orientation (111) crystallite size variation with increasing Cu doping concentration (34.92, 34.02, 30.87, 30.81, 32.35, 34.04)nm respectively, and lattice constant was (8.065, 8.0668, 8.0692, 8.074, 8.0854, 8.0546)A°. It is found from optical measurements that the transmition is inversely proportional with concentration, the absorption coefficient (α) at the fundamental absorption region was determined using the spectra data of transmittance. The tow allowed direct energy gaps were varied between (1.4 to 2.06) eV and they are decreasing with increasing the doping concentration. While the two indirect energy gaps were decrease as doping concentrations were increased with variation between (1.2 to 1.9) eV.

KEYWORDS: thin films, spray pyrolysis, doping, Co_3O_4, CuO.

INTRODUCTION
Transition metal oxides (TMOs) consider as an important and promising materials which have attracted large attention in many technological applications due to their outstanding electronic, optical, magnetic, and catalytic properties [1,2]. Cobalt oxides are one of the most important transition oxides which has huge interest in several fields. It is a p-type cubic spinle structure semiconducting material with two direct and indirect optical bandgaps (1.44-2.06) eV and (1.26-1.38) eV respectively, Bulk cobalt oxide crystals appear in two stable crystallographic structures, the rocksalt-type CoO and the normal-spinel-type Co_3O_4 . CoO phase has a high chemical stability but it easily oxidised to Co3O4 in the open air atmosphere so at last years many researches widely studied Co_3O_4 phase in open air atmosphere as promising materials due to its chemical stability, an antiferromagnetic material with mixed valence (Co3+ and Co2+ ion) and regular spinel structure having Co3+ in Octahedral sites and Co2+ in Tetrahedral sites. It is a material widely employ in various emerging applications like Supercapacitor, Gas sensor, solar selective absorber, Lithium ion battery, etc.[3, 4, 5, 6]. Both Co3O4 and CoO exhibit a cubic lattice and usually nonstoichiometric with excess oxygen, leading to p-type semiconducting behaviours [7]. Copper oxide which is considered as one of the most important p-type semiconductor transition metal oxide which exists in two general phases: cupric oxide (CuO) and cuprous oxide (Cu_2O) [8]. CuO (copper (II) oxide) Cupric Oxide is belongs to the monoclinic crystal structure with energy bandgap of (1.2-2.1) eV. On the other hand, Cu_2O (copper (I) oxide) cuprous oxide is belongs to the cubic crystal structure with energy bandgap of (2.2-2.9) eV [9]. Cobalt oxide thin films can be prepared by using various liquid and vapour phase methods such as chemical vapor deposition (CVD), spray pyrolysis, electrodeposition [10, 11], thermal decomposition, puls laser deposition, sol-gel [2]. Among the various deposition techniques, the spray pyrolysis is the most suitable method for the preparation of doping thin films because of its simplicity, inexpensive experimental arrangement, ease of adding various doping materials [12]. Therefore, the aim of the work is variation of structural and optical properties of Co_3O_4 thin films by doping with different concentrations of Cu doping by spray pyrolysis.

EXPERIMENTAL
Copper-doped cobalt oxide thin films are prepared by sprayed an aqueous solutions of $CoCl_2.6H_2O$ mixed with different percentage of $CuCl_2.6H_2O$ (0%, 1%, 3%, 5%, 7%, 9%) M. The mixed chlorides were dissolved in

distilled water by using a magnetic stirrer until the solution became clear then it sprayed towards the glass substrate with a distance of about ~30 cm. The flow rate of the solution during spraying was adjusted about 10 ml/min and kept constant throughout the deposition. The temperature of the substrate was measured by thermometer and kept at (350) ^{O}C.

The structural properties were studied by X-ray diffraction measurements (Shimzu X-Ray Diffract meter XRD 60000). Optical transmittance with respect to glass substrate measurements were carried out within the wavelength range from (300-1100) nm by using UV-Visible Spectrophotometer (UV-1800). From the transmittance we can calculate the absorption coefficient and energy band gap.

RESULTS AND DISCUSSION
structural properties
The structural properties of thin film is the key to recognize its quality. X-ray diffraction of copper-doped cobalt oxide thin films with different Cu/Co ratio (1- 9) % shown in figure (1). It is illustrate that all films have a polycrystalline structure of Co_3O_4 with peak of perfect orientation plane (111) at 2θ=(19.046) and position of this (2θ) decreas with Cu ratio increase.The existence of another peak at 2θ= (19.040, 19.035, 19.272, 18.996, 19.069) deg could be denoted to a cubic spinel lattice of Co_3O_4 phase as identify with ICDD data card No. (042-1467). it is observed peaks with orientation planes (111), (222) and (400) be stronger with increasing of Cu ratio in Co_3O_4 thin films. thus the changing in Cu doping ratio result in variation of the preferred growth.
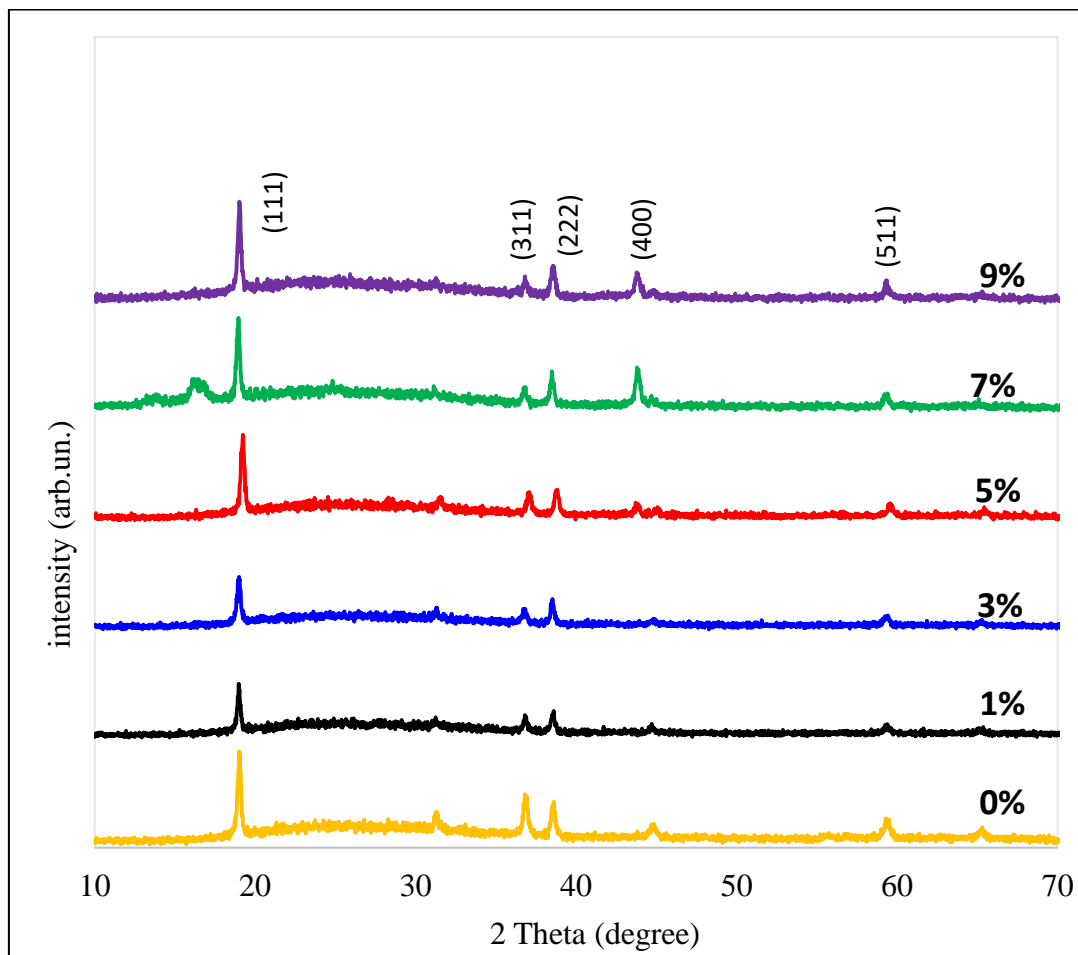

Figure (1): XRD patterns of Cu:Co₃O₄ thin films prepared with different concentration of Cu doping: (0%, 1%, 3%, 5%, 7%, 9%) M at Temp.(350 ºC).

No phase corresponding to copper or other copper compound were detected in the XRD pattern. In general the intensity of peaks were increased with increasing molar concentration of dopping in which indicated that the films

crystallinity have been improved as mentioned by A. La Rosa et.al. [2]. The crystalline parameters like lattice constant (a), crystallite size (D), dislocation density (δ), and micro strain (ε) were determine from XRD data and illustrated in table (1). An analysis has been carried for the preferred orientation plane (111) of the investigated thin films. The lattice constant (a) of doped thin films werre calculated according to the equation [3]:

$$d_{hkl} = \frac{a_\circ}{\sqrt{h^2+k^2+l^2}} \qquad ....(1)$$

Where (d) illustrate the distance between lattice planes h,k,and l denotes to miller indices (111). The values of lattice constant are close to the reported value in research which varied between 7.78 to 8.005Å. [3]

For all films the crystallite size (D) was determine from the full width at half maximum (FWHM) of the preferred orientation diffraction peak (111) by using Scherrer equation as shown below [13]:

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

Where (K) is the shape factor equal to (0.94), (λ) is the Cu=Kα radiation wavelength (1.5406 A˚), (β) refers the full width half maximum (FWHM) in radians, and (θ) is the angle of incidence radiation. It is noted from Table (1) that the increasing in doping concentration leads to decrease the crystallite size and this agreement with XRD results. it is clear that the peaks intensity decreased at doping ratio (1, 3, 5)%, and then increased at ratio (7,9)% which denoted to enhancement of crystallinity of thin films .

To get more crystal quality information, dislocation density must be determine according to the relation [3]:

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

The dislocation density is the length of dislocation lines per unit volume of the crystal. Larger D and smaller δ values mean better crystallization of the films [13]. Dislocation densities exhibit variation with increasing doping concentrations. From table (1) we notice that when D decrease in ratio (1,3)% of Cu, the dislocation increase reach to ratio 5% Cu , after that D increase and the dislocation will decrease because of improving of crystallinity.

In thin films, strain originate mainly from the mismatch between the polycrystalline film and the amorphous substrate and or from the difference in the thermal expansion coefficient of the film and the substrate, micro strain can be calculated by using the formula [14]:

$$\varepsilon = \frac{\beta \cos\theta}{4} \qquad ....(4)$$

table (1) reflect the increasing in microstain with increased Cu/Co ratio up to 5% after that it is decreased due to good crystallinity of this film as noticed from XRD results.

Table(1) :The crystal parameters of Cu:Co₃O₄ thin films prepared with different doping concentration at (T=350 C˚).

Doping	hkl	2θ (deg)	FWHM (deg) β	d spacing (A°)	D Crystallite size (nm)	a lattice constant (A°)	δ Dislocation density (line/m²)*10¹⁸	ε macrostrain (line⁻² m⁻⁴)*10³
0%	111	19.043	0.2409	4.656	34.924	8.0653	0.819	1.036
1%	111	19.040	0.2473	4.657	34.0203	8.0668	0.864	1.064
3%	111	19.034	0.2725	4.658	30.874	8.0692	1.049	1.1726

5%	111	19.272	0.2731	4.661	30.8169	8.0745	1.052	1.174
7%	111	18.996	0.260	4.668	32.357	8.0854	0.955	1.118
9%	111	19.069	0.2471	4.650	34.0493	8.0547	0.862	1.063

Optical Properties

In order to investigate the influence of copper presence on the optical properties of Co_3O_4 thin films, the optical transmission of Cu doped Co_3O_4 thin films were measured. Figure (2) shows the variation of optical transmission (T) of $Cu:Co_3O_4$ thin films as a function of wavelength at various concentration of Cu doping. it is found that the transmission is increased with increasing of wavelength and decreased with increasing of doping concentration, and for all thin films there is region of transmission increasing at wavelength (625 and 1100)nm, and this a natural behavior of Co_3O_4 .

the highest values of transmission was (52%, 56%, 48%, 37%, 33%, 32%) for concentration (0%, 1%, 3%, 5%, 7%, 9%) at (1100 nm) wavelength respectively and this may be due to the structural and surface effect. This behavior can be attribute to : better crystallinity, less surface irregularity, defect density.
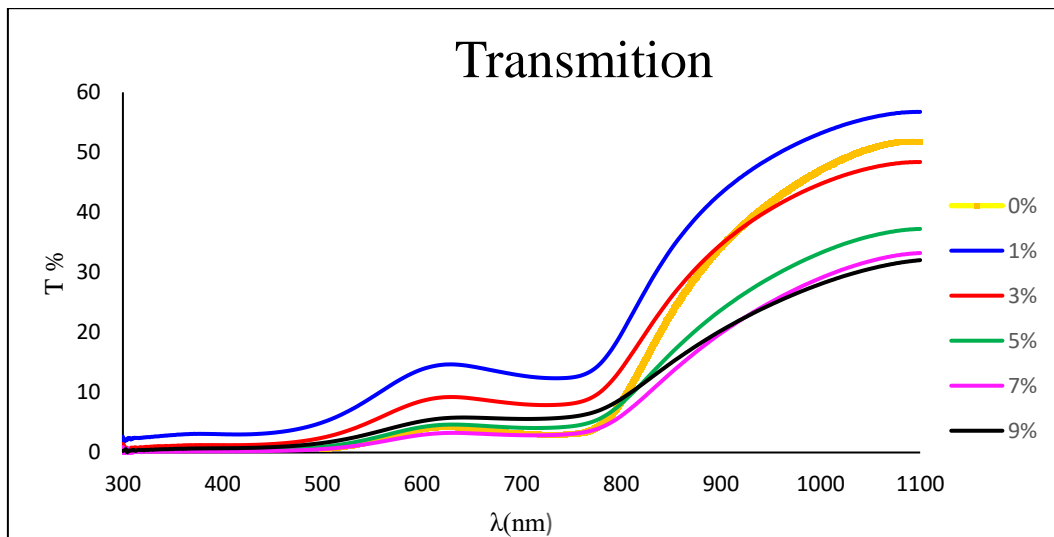

Figure (2): transmission as a function of wavelength for Cu :Co₃O₄ thin films with different concentration at (350)C°.

Figure (3) shows the variation of the absorption coefficient (α) of $Cu:Co_3O_4$ thin films as a function of wavelength (300-1100) nm at various concentrations of Cu doping. The optical absorption coefficient (α) of the films can be calculated using the following equation [3]:

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \qquad \ldots\ldots\ldots\ldots (5)$$

where (t) is the film thickness (319 nm) and (T) is the transmission of the film. It is found that there is a red shift in absorption edge to higher wavelength (700-800) nm with increasing Cu concentration. The figure display that absorption coefficient variation with increase the concentration, (7%) have the highest absorption coefficient at (750)nm wavelength due to its low transmission, and good crystalline structure
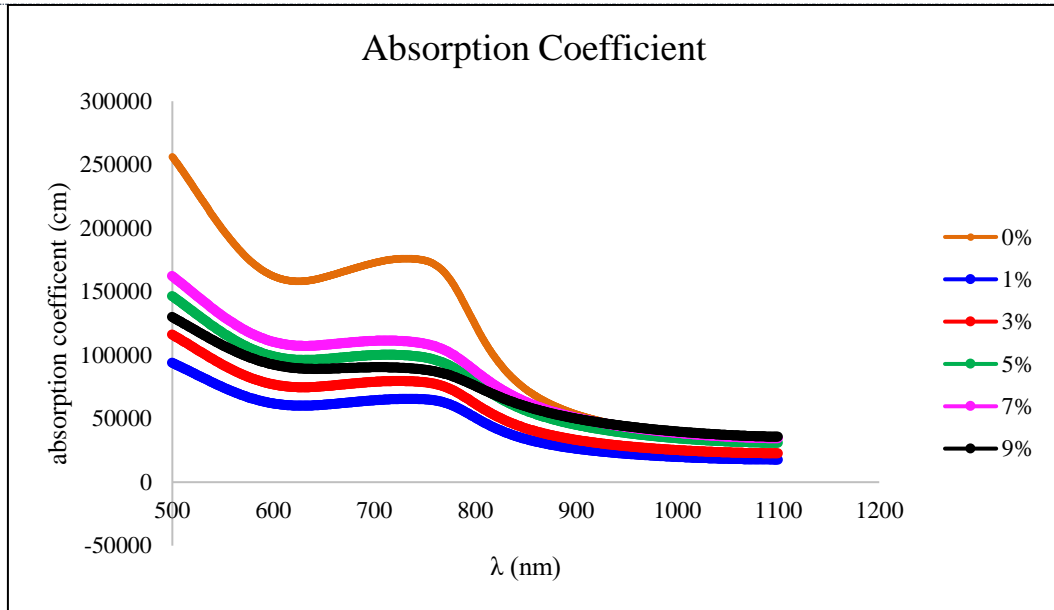
Figure (3): the absorption coefficient of CuxCo3-xO4 tin films as a function of wavelength for different doping concentration

In order to realize the kind of the optical transition direct or indirect allowed or forbidden, the optical absorption data were analyzed the famous relation between (α) and photon energy in semiconductor which known as Tauc relation[15] :

$$\alpha = \alpha_o \, (h\upsilon - E_g)^n / \, h\upsilon \quad \ldots\ldots\ldots(6)$$

where α_o is constant, $h\upsilon$ is the photon energy and E_g is the energy band gap, (n) is constant that depended on the optical transition and equal to (0.5, 2) for allowed direct and indirect transition, respectively [3]. Figure (4) illustrate the methode to determine the direct energy band gap (Eg) values for Cu :Co$_3$O$_4$ films with different doping concentration by plotting $(\alpha h\upsilon)^2$ versus photon energy (hυ). The figure reflect the existence of two linear portion in the curve and this mean two value of energy band gap was find. [15]. Figure (5) illustrate the methode to determine the indirect energy band gap (Eg) values for Cu :Co$_3$O$_4$ films with different doping concentration by plotting $(\alpha h\upsilon)^{1/2}$ versus photon energy (hυ). The value of the direct and indirect energy gap values are given in table (2). It is found that Eg decrease with increase concentration due to the decreasing in the crystalline size and increasing in the carrier density of material as explained by [2, 13, 14] .

Table (2): energy gab of thin film with different doping concentration for direct and indirect energy gaps

concentration of %Cu doping	direct energy gap (Eg1, Eg2) (ev)		indirect energy gap (Eg1, Eg2) (ev)	
0%	1.48	2.06	1.42	1.92
1%	1.46	2.04	1.32	1.66
3%	1.44	2	1.32	1.64
5%	1.42	1.98	1.28	1.56
7%	1.41	1.96	1.26	1.56
9%	1.4	1.93	1.32	1.64
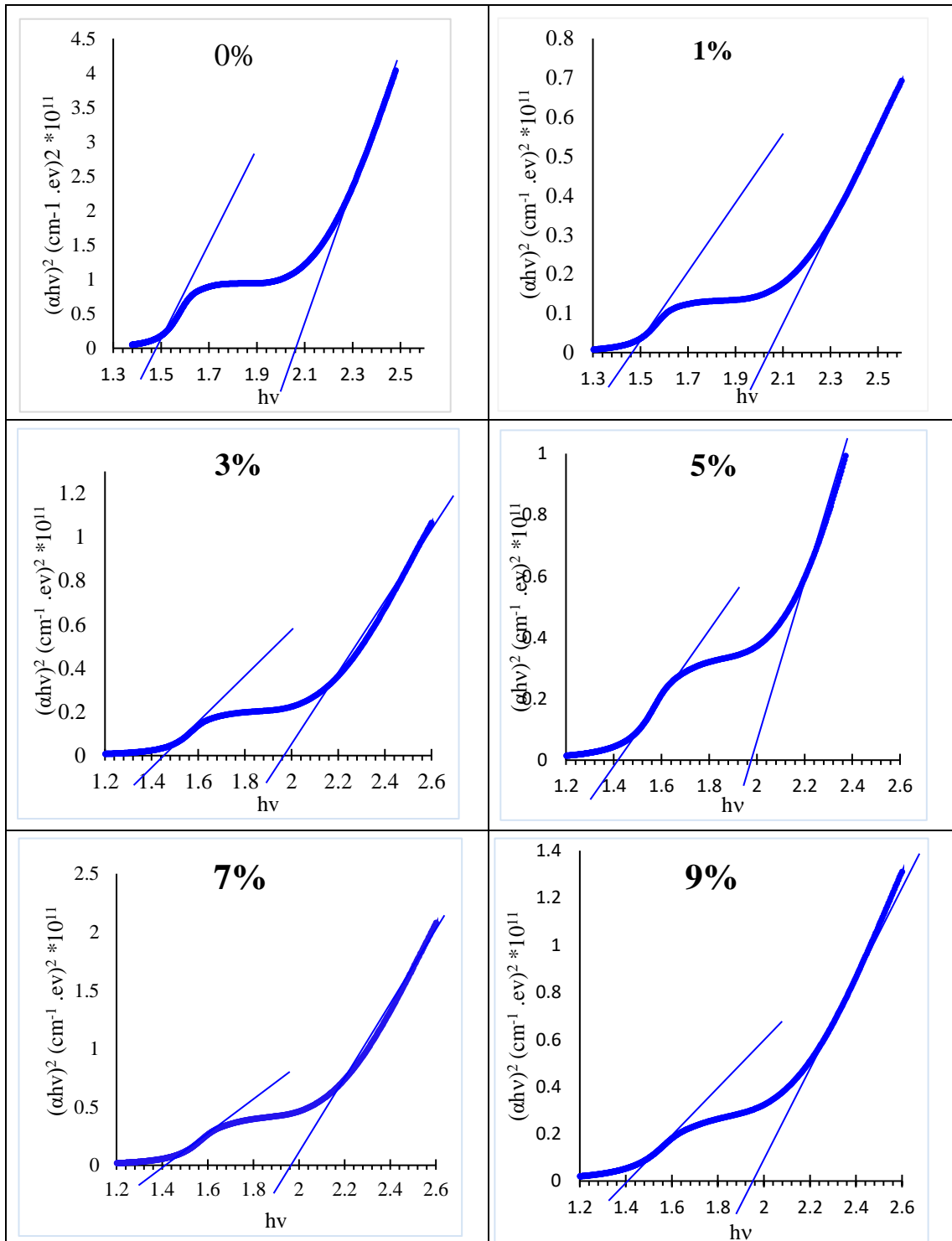
Figure(4) : allowed direct energy gaps for different concentrations .
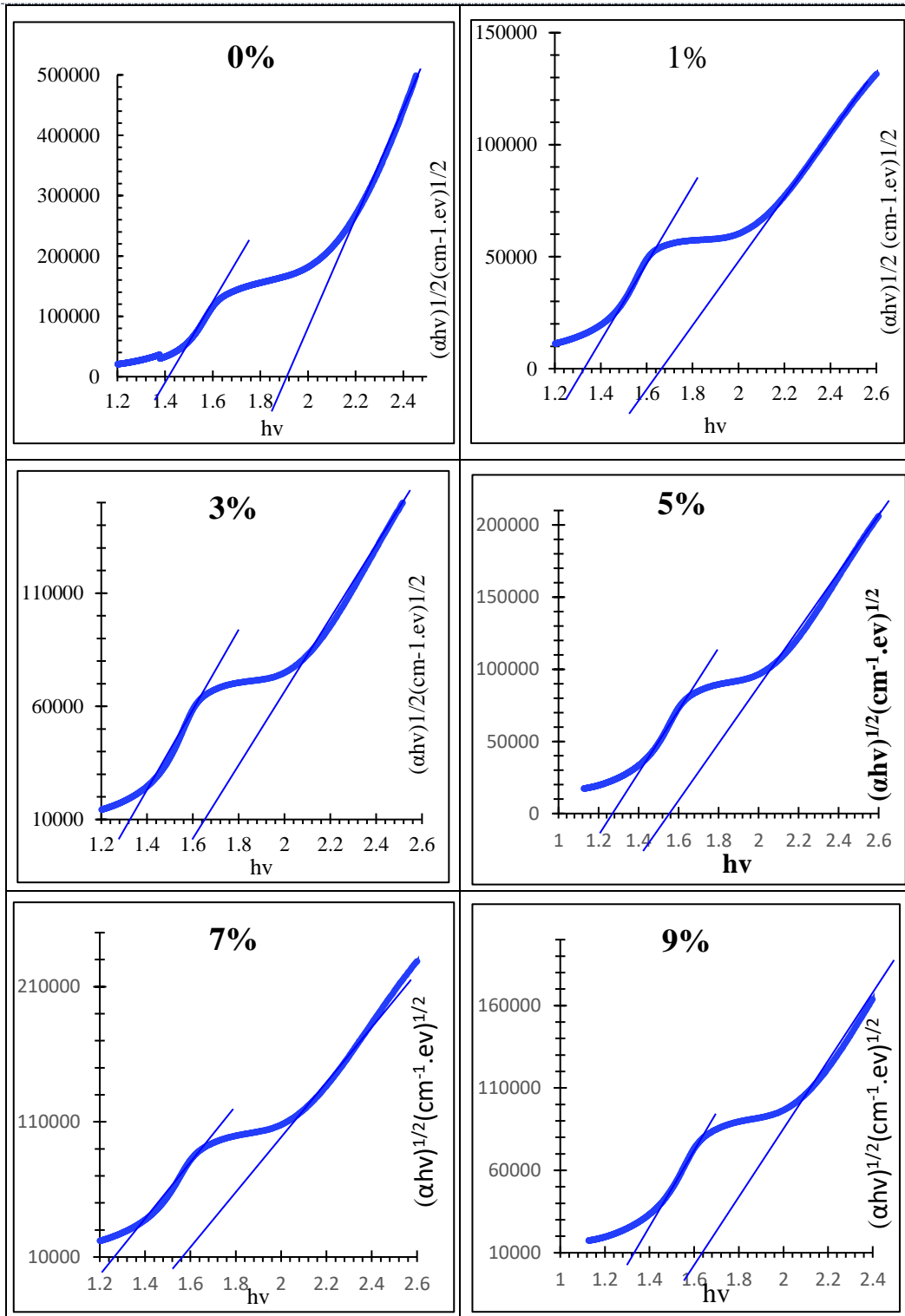
Figure (5): the optical indirect allowed energy gap at different concentrations.

EXTINCTION COEFFICIENT (K)

The extinction coefficient (k) which is defined as the amount of electromagnetic wave energy lossing when it pass through material, it is related with the wavelength (λ) and absorption coefficient (α) by the following equation [15] :

$$K = \frac{\lambda \alpha}{4\pi} \qquad \dots\dots\dots\dots\dots\dots \ (7)$$

Figure (6) show The variation of the extinction coefficient (K) as a function of wavelength for various doping concentrations (0%, 1%, 3%, 5%, 7%, 9%) M. it is observed that the extinction coefficient decrease with wavelength and increase with increasing of concentration and the peak was in the visible region at wavelength(760)nm) indicate high absorption at this region and begin to decrease in near infrared region which reflect similarly to absorption coefficient behavior and this shown by other researchs [15, 16].
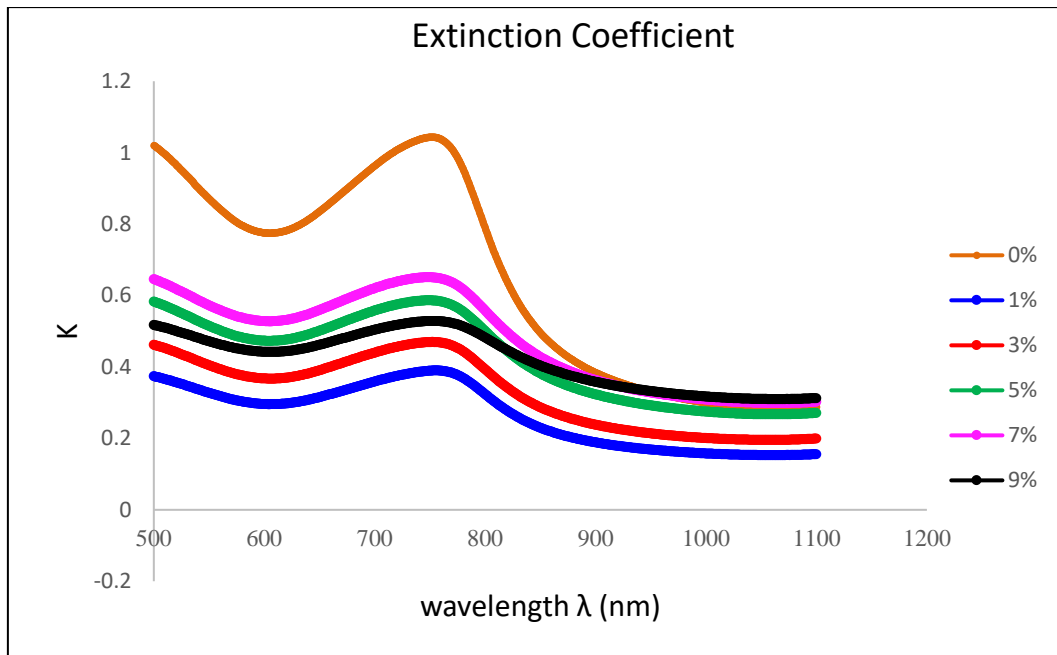
Figure(6): shows the relation between extinction coefficient and wavelength with different doping concentration of Cu :Co₃O₄ thin films.

CONCLUSION
Single phase of (Cu :Co$_3$O$_4$) is important in the application of delafossite thin film. (Cu :Co$_3$O$_4$) phase were successfully prepared by spray pyrolysis method at substrate temperature 350 ºC with different doping concentration of precursor solution (0%, 1%, 3%, 5%, 7%, 9%) M. X-ray diffraction reflect the formation (Cu :Co$_3$O$_4$) of spinel structure of cubic unit cell and average lattice constant (8.08 Aº) with good crystallinity. The grain size increase with the concentration while the micro strain and dislocation decrease with. Optical measurement indicate the presence of two value of energy gap for direct and indirect transition, where as decrease with concentration.

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