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Synthesis and Characterization of Hg$_{1-x}$Cd$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ thin film Superconductors prepared by DC Sputtering

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Abstract: Mercury-cadmium base Superconductors with formula Hg$_{1-x}$Cd$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ with (x=0.1, 0.2 and 0.25) thin films have been prepared on glass substrate at R.T (300 K) with 178 nm thickness using DC sputtering technique by two step, the first step (bulk) by solid state reaction processes and the second step thin film. The influences of Cd content on the structural and optical properties were investigated. Structural analysis results from the X-ray diffraction (XRD) and Atomic force microscope (AFM) techniques indicate that all samples are polycrystalline of multiphase with tetragonal structure and have a grain size of (80-45) nm. It was found that the increasing of the cd content ratio in samples produce changes on the lattice constant, volume fraction (V$_{phase}$),grain size. The transmission and absorptions spectrum of these films as a function of wavelengths in the range (300-1100) nm were used to study the optical properties and calculate the optical constants such as absorption coefficient, refractive index, extinction coefficient, real and imaginary parts of the dielectric constant, also the optical conductivity were investigated and calculated.

Key words: Hg$_{1-x}$Cd$_x$Ba$_2$Ca$_2$Cu$_3$O$_{8+\delta}$, Superconductors, Structural properties, Optical Properties.

INTRODUCTION

The period from 1994 up to now has been very fruitful for the synthesis of new high transition temperature superconductor compound (HTSC)[1]. A significant success has been achieved in the synthesis of large a group of mercury-containing HTSC, which have the highest critical temperatures of the superconducting[2,3]. The general formula for the homologous series of Hg-based is given by $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ where n is the number of CuO_2 layers per unit cell. High sensitivity as well as chemical instability and week flux-pinning behavior based on Hg make synthesis of $HgBa_2Ca_2Cu_3O_{8+\delta}$ by any method difficult in forming a single superconducting phase .Therefore, this compound consists of a mixture of $HgBa_2Ca_1Cu_2O_{7+\delta}$ (1212) and $HgBa_2Ca_2Cu_3O_{8+\delta}$ (1223) phases, because the 1212 phase is thermodynamically more favorable at elevated temperature than the 1223phase[4].Studied a model of n-layer high-temperature cup rates of homologous series like $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ to explain the dependence of the critical temperature $T_c(n)$ on the number n of Cu-O planes in the elementary cell[5], and measured the pressure sensitivity of T_c in fluorinated $HgBa_2Ca_2Cu_3O_{8+\delta}$ ceramic sample with different (F) contents ,applying pressures up to 30 GPa . They obtained an increase of T_c with the increase of pressure, reaching different maximum values, depending on the F doping level, and pressures. High $T_c= (166\pm1)$ K was achieved by applying 23 GPa in fluorinated Hg-1223 sample near the optimum doping level[6]. Prepared HTSC with a nominal composition Hg_{1-x} $(Ag,In)_x$ Ba_{2-y} Sr_y $Ca_2Cu_3O_{8+\delta}$ for ($0 \le x \le 0.5$) and ($0 \le y \le 0.5$) by a solid state reaction method. The effect of the substitution of (Ag, In)on Hg sites and S_r for Ba sites, sintering time, sintering temperature and γ-irradiation has been investigated to obtain the optimum conditions for the formation and stabilization of the high T_c-1223 phase. She found that substitution of Ag and S_r together enhances T_c to 127 K at x=0.2 and y=0.1, while for the samples substituted with In and S_r together give T_c=125 K at x=0.3 and y=0.1. XRD analyses have showed a tetragonal structure and there is an increase of c-lattice parameter with increasing of Ag up to 0.3, while samples doped with In have showed a decrease in c-lattice parameter[7]. Different techniques have been used by different workers to prepare superconducting thin films, such as chemical vapor deposition[8], laser ablation[9], molecular beam epitaxy[10], co-evaporation [11], metal organic chemical vapour deposition (MOCVD)[12], magnetron sputtering[13] and the excimer laser etching[14]. In the present paper, we prepared and study the effect of Cd content on the structural and optical properties of superconducting $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ thin films with (x = 0.1, 0.2 and 0.25) prepared by D.C. sputtering.

EXPERIMENTAL

The $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ with (x=0.1, 0.2 and 0.25) high critical temperature superconducting (HTS) thin films were fabricated using two-step process (bulk and thin film). At first the precursor bulk was prepared by solid state reaction, using appropriate weights of pure powders materials HgO,CdO, BaO,CaO and CuO, and in proportion to their molecular weights. The weight of each reactant was measured by using a sensitive balance whose sensitivity is of the order (10^{-4}) gm. The powders were mixed together by using a gate mortar; a sufficient quantity of 2- propane was to homogenization the mixture and to form slurry during the process of grinding for about (40-60) minute. The mixture was put in alumina crucible and dried for an oven at 150°C. The powder was pressed into disc-shape pellets (1.3 cm) in diameter and (0.2-0.3) cm thick; using hydraulic press under a pressure of (6 ton/cm^2).The pellets were put in a furnace which has programmable controller for sintering. The pellets were sintered in air at (855-860)$^{\circ}$C for (12 h) with a rate of (60 $^{\circ}$C/h) and then cooled to room temperature by the same

rate. In the second step, the pellets were used as a target to prepare thin film compound on a slide glass, by using D.C. sputtering technique. Cathode voltage was ranging between 2-3 KV. The distance between the target and the substrates was 4 cm. The background pressure of the chamber was 10^{-4} torr. Argon gas was introduced through a needle valve to about 10^{-2} torr for creation the glow discharge. After running the system for 4 hours, one will obtain thin film samples with thickness of 178 nm.The execs of oxygen content (δ) as well as the critical temperatures measurements were carried out using the four - point technique and the volume fraction of any phase (V_{phase}) have been described elsewhere[15]. Crystal structure such as phase crystalline, polycrystalline, amorphous, grain size, and lattice parameter of all samples prepared have been examined using X-ray diffraction (XRD) technique using X-ray diffractometer system (SHIMADZU Japan XRD 600) by records the intensity in the range of Bragg's angle θ from (20-60), source Cu K_{α} radiation of wavelength (λ=1.5405 Å) was employed with generator setting of current 20 mA and voltage 40 kV. The surface morphology of these samples observed from the Atomic force microscope (AFM) technique, by using SPM model AA3000 contact mode spectrometer, supplied by Angstrom Advanced Inc. Company, USA. to determine the nanocrystalline topography. Optical properties measurements of these films grown on glass substrates were studied by recorded the transmittance (T) and absorbance (A) spectrum in the range of wavelengths (300-1100) nm using a double beam spectrophotometer (UV/VIS), to determine the optical parameters such as reflectance (R), absorption coefficient (α), optical energy gap (Eg^{opt}), refractive index (n), extinction coefficient (K), and dielectric constant (ε).

RESULT AND DISCUSSION

Structural Properties: The X-ray diffraction pattern of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ samples with (x=0.1, 0.2 and 0.25) are shown in Fig.(1). We can deduce from this figure that all the samples have polycrystalline nature with tetragonal phase formation. The peaks are observed due to diffraction from different planes shows mixed phases.
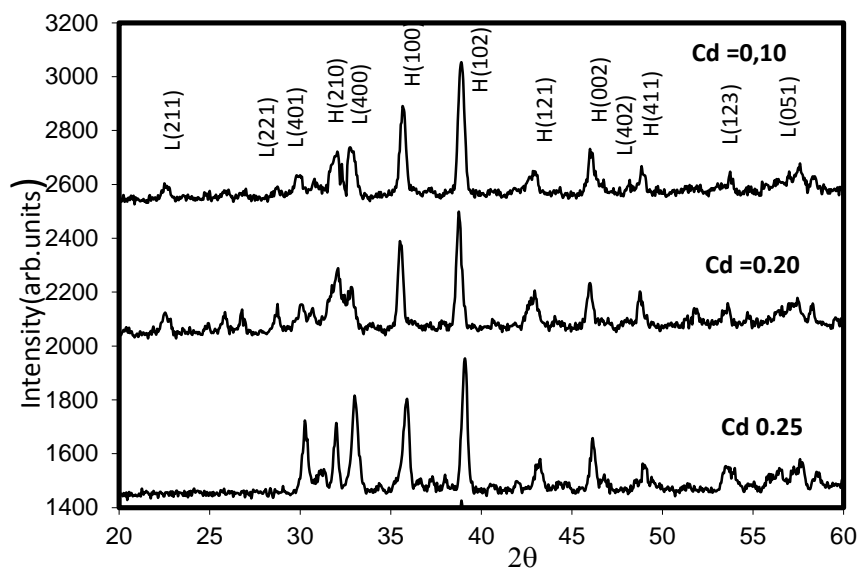

Fig.1: X-ray diffraction pattern of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ (x=0.1, 0.2 and 0.25)

For the stoichiometric nominal composition of the $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ samples, it was found that content a high phase (Hg(Cd)-1223) and low phase (Hg(Cd)-1212) and some impurity phases of Ca_2CuO_3, $CaBaO_4$ and $CaCuO_4$ with vanishingly small concentrations of unknown phases. This result indicates that the formation of the Hg-2223 phase is increased with the increase Cd. From date XRD diffraction, The lattice constants (a) and (c) calculated from the relation[16]:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l}{c^2} \qquad\qquad \dots (1)$$

Using a computer program, this program based on Cohen's least square method, where d (hkl) is the inter planer distance for different planes which estimated from Bragg's law[9]:

$$2d\sin\theta = n\lambda \qquad\qquad \dots (2)$$

Where n is the reflection order.

These data of transition temperatures ($T_{c\,(offset)}$), a, b, c/a and volume fraction of high phase V_{2223ph} as shown in Table 1. It is clear from this table that $Hg_{1.9}Cd_{0.1}Ba_2Ca_2Cu_3O_{8.31}$, $Hg_{1.8}Cd_{0.2}Ba_2Ca_2Cu_3O_{8.28}$ and $Hg_{1.75}Cd_{0.25}Ba_2Ca_2Cu_3O_{8.23}$ samples, are superconductors with critical transition temperatures ($T_{c\,(offset)}$) 119, 125, and 129 K, respectively, and there is an increase of a-lattice parameter with increasing of Cd content up to 0.25, while showed a decrease in c-lattice parameter

Table-1: lattice parameter and volume fraction V_{2223ph} for $Hg_{1.9}Cd_{0.1}Ba_2Ca_2Cu_3O_{8.31}$, $Hg_{1.8}Cd_{0.2}Ba_2Ca_2Cu_3O_{8.28}$ and $Hg_{1.75}Cd_{0.25}Ba_2Ca_2Cu_3O_{8.23}$

X	$T_{c(offset)}$ (K)	a($\dot{A}$)	c($\dot{A}$)	c/a	V_{2223ph}
0.1	119	3.3463	15.994	5.130	77%
0.2	125	3.3758	15.389	5.129	81%
0.25	129	3.3951	15.091	5.111	83%

The surface morphology of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ films where (x=0.1, 0.2 and 0.25) was observed using AFM. Figure 2 shows the AFM images of these films deposited on glass substrate, the values of average size range were found to be dependent on the Cd content with (80,60 and 45) nm respectively. These images show that these films are homogeneous, uniformly distributed features with no pinholes or island structure.
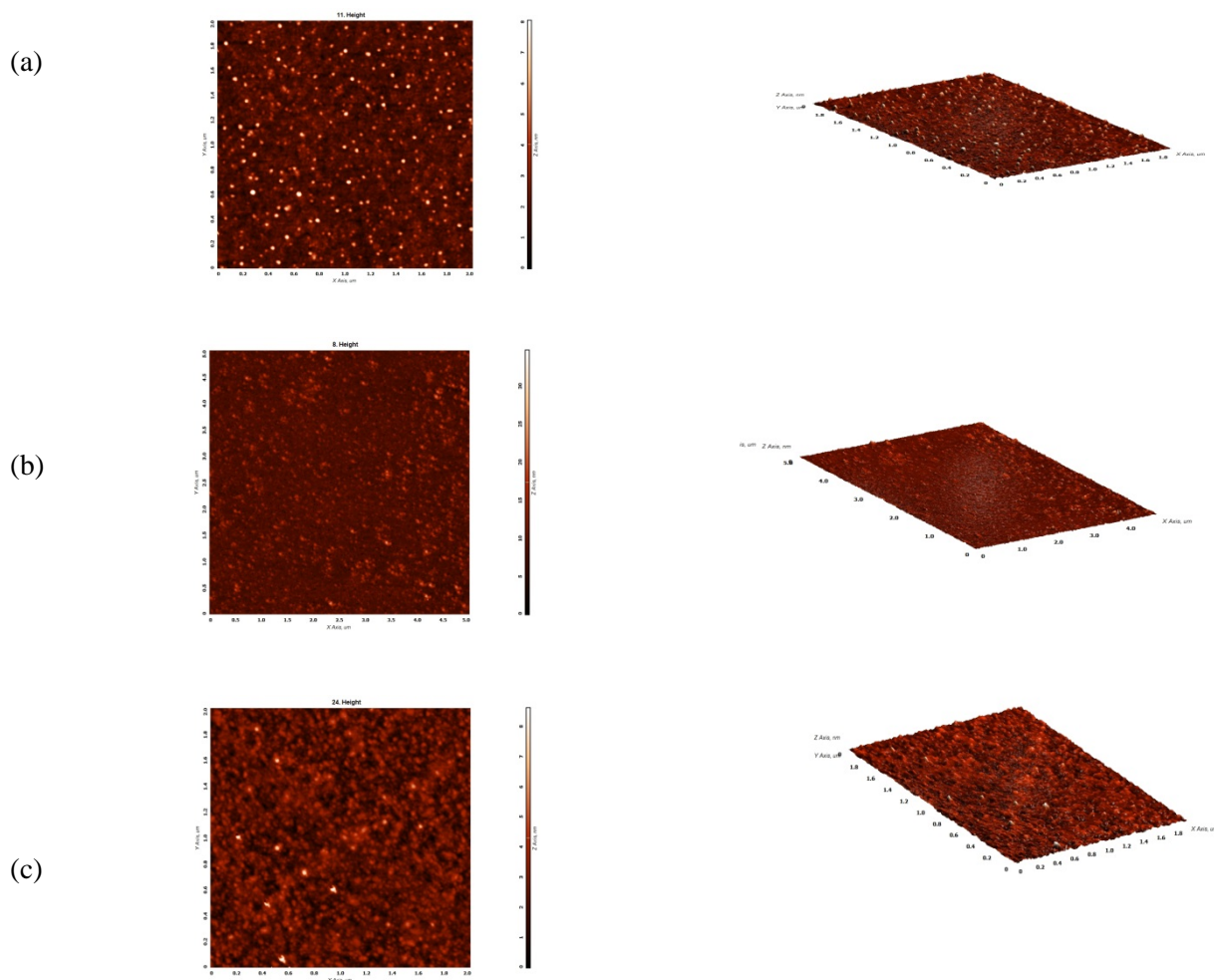
Fig. 2: 2D &3D AFM images of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ for a) x=0.1; (b) x=0.2; (c) x=0.25

Optical Properties: The influence of ratio Cd content on the optical properties of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ thin films for (x=0.1, 0.2 and 0.25) are investigated within the wave length range (300 – 1000) nm. Fig. (3) shows the variation of absorbance (A) as a function wave length range .We could see from this figure that the absorbance values increase followed decreased these value generally as the wave length increases and these samples have low values in the NIR region, can be also observe that these films exhibit an absorption edge and it is shifts to lower wavelength with increase Cd concentration. It is clear from this figure that the value of the absorbance of these films decreased with increase the Cd content percentage in the sample for all values of the wavelength attributed to that Cd introduces inter band energy levels in the band gap of these films which make a stronger interaction among them and this behavior can be attributed to the change in the films structure with increasing Cd content ratio due to decrease the absorbance values; we deduce that the absorption is not attributed to the free carriers only, but to impurities or localized electronic states.
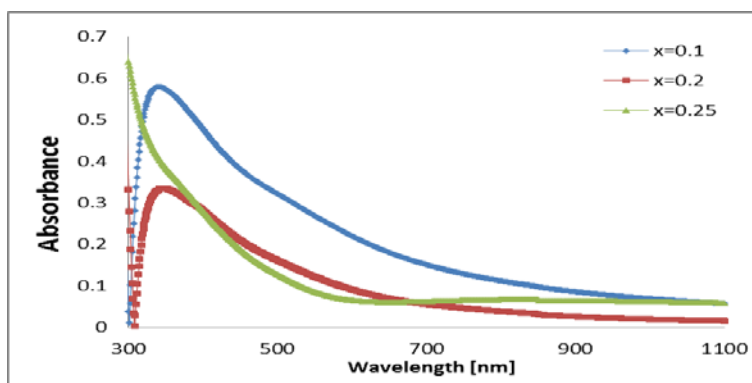
Fig.3: absorbance verses wave length of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ films as a function of Cd content (x=0.1, 0.2 and 0.25)

Transmittance values verses wave length with the range (300 – 1000) nm of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ films as a function of Cd content (x=0.1, 0.2 and 0.25) are shown in fig (4), from this figure we can notice that the transmittance values increased generally as the wave length increases and have high values in the NIR region, all samples demonstrate above (65 - 90) % transmittance at wavelengths longer than 700 nm which makes these films suitable for solar energy collection. The transmittance (T) values which calculated from the relation[16]:
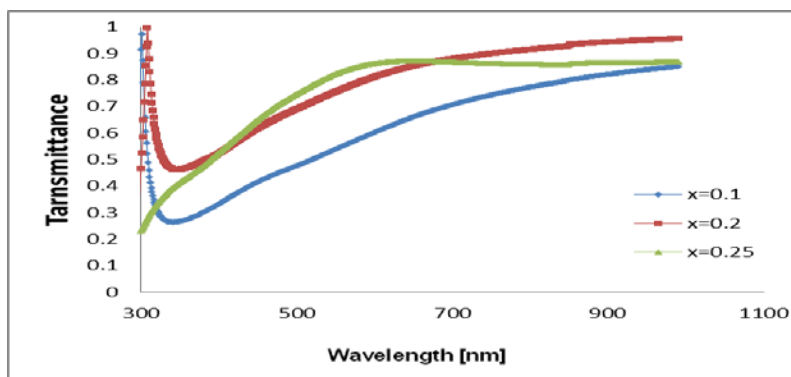
$$T = 10^{-(A)} \qquad \qquad \dots (3)$$

Fig.4: transmittance verses wave length of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ films as a function of Cd content (x=0.1, 0.2 and 0.25)

Fig (5) shows a plot of the reflectance values R versus wavelength range (300 – 1000) nm for $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ thin films which calculated by using equation:

$$R = 1-T-A \qquad \qquad \dots (4)$$

It is clear from this figure that the value of the reflectance of these films decreased with increase wave length and Cd content percentage in the sample. This behavior can be attributed to the difference in the nature of this film surface.
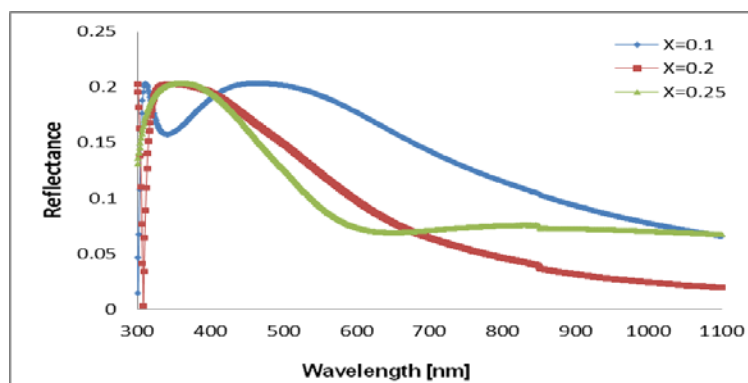
Fig.5: reflectance verses wave length of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ films as a function of Cd content (x=0.1, 0.2 and 0.25)

The absorption coefficient (α) calculated from the relation[16]:

α = 2.303 (A / t)   ……… (5)

Where t is film thickness.

It is notice from figure (6) the variation in the absorption coefficient values α of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ thin films for (x=0.1, 0.2 and 0.25) verses incident photon energy (E=hν) which calculated as a function of wavelength (λ) from equation:

E (eV) = 1240 / $\lambda_{(nm)}$ ……… …(6)

The absorption coefficient values increase with increasing photon energy while it decrease with increase Cd content in films within the whole range of the spectrum. This behavior may be due to the variation crystal structure of these films, can be also notice from this figure that all the films have high values of absorption coefficient ($\alpha > 10^4$ cm^{-1}) this means that the direct transition is possible occurs.
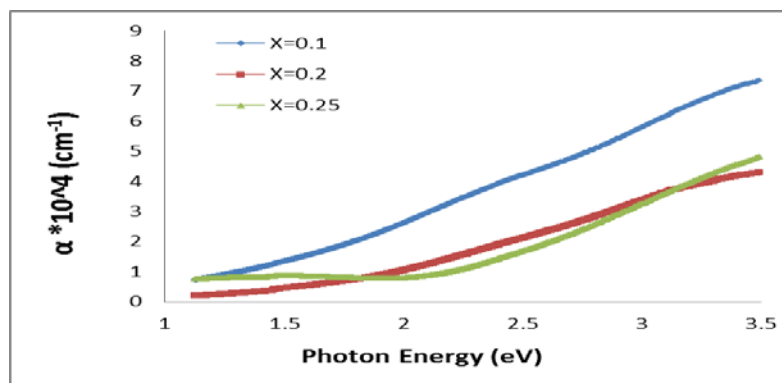

Fig.6: Absorption coefficient behavior verses photon energy of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ films as a function of Cd content (x=0.1, 0.2 and 0.25

The optical energy gap (Eg^{opt}) can calculated from Tauc equation[17] :

$$(\alpha\ h\nu) = B\ (h\nu - Eg^{opt})^r \quad \dots (7)$$

Where B is a constant, r is constant and may take values 2, 3, 1/2, 3/2 depending on the material and the type of the optical transition. It can be find the type of the optical transition for all samples by plot $(\alpha\ h\nu)^2$ versus photon energy (hν) Fig (7) , which describes the allowed direct transition and calculated the optical energy gap (Eg^{opt}) by select the optimum linear part, which determined by the extrapolation of the portion at (α =0).It is clear from this figure the optical energy gap increase when the Cd content increased in film, were found to be 2.3,2.5 and 2.75eV for x=0.1,x=0.2 and x=0.25 respectively. This behavior can be attributed to the decrease of the density of localize states in the Eg .
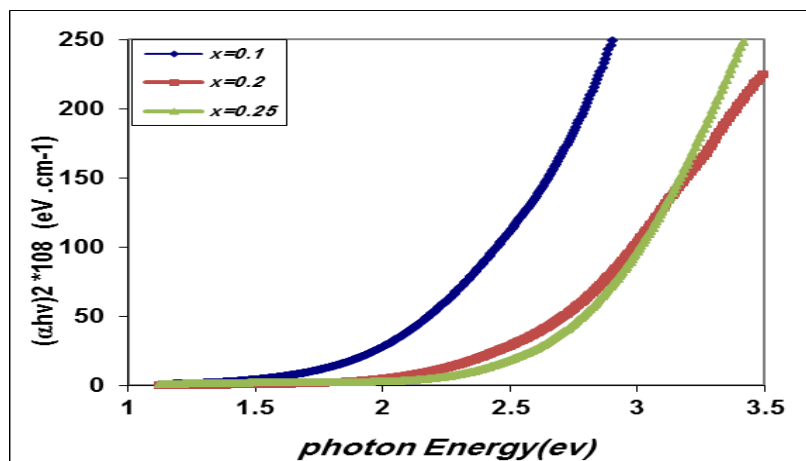

Fig.7: $(\alpha\ h\nu)^2$ versus photon energy (hν) of $Hg_{1-x}\,Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ films as a function of Cd content (x=0.1, 0.2 and 0.25)

Fig (8) shows the variation of the extinction coefficient K versus photon energy for $Hg_{1-x}\,Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ thin films for (x=0.1, 0.2 and 0.25), which obtained using the relation[17]:

$$K = \alpha\ \lambda\ /\ 4\pi \quad \dots (8)$$

It can be seen from this figure that the extinction coefficient behavior nearly similar for all the range of the wavelength spectrum to that of the absorption coefficients, this means the extinction coefficient values decrease with increase Cd content in films for the same reasons as we mentioned before .
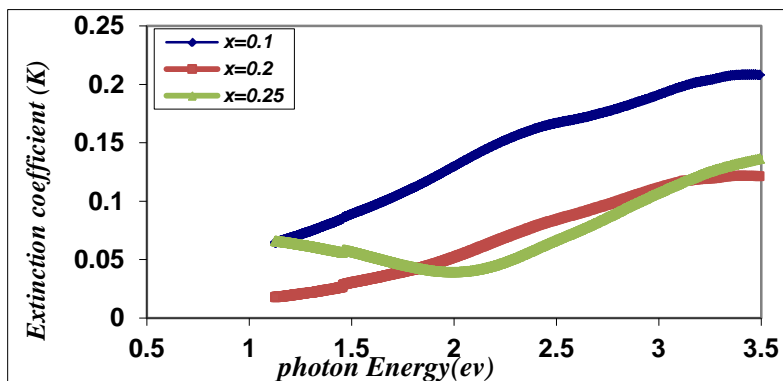
Fig.8: Extinction coefficient behavior verses photon energy of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ films as a function of Cd content (x=0.1, 0.2 and 0.25)

It can be seen from the Fig (9) the variation of the refractive index values n versus photon energy for $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ thin films for (x=0.1, 0.2 and 0.25), which calculated from equation[18]:

$$n = \left[\left(\frac{1+R}{1-R}\right)^2 - (K^2+1)\right]^{1/2} + \frac{1+R}{1-R} \qquad \ldots (9)$$
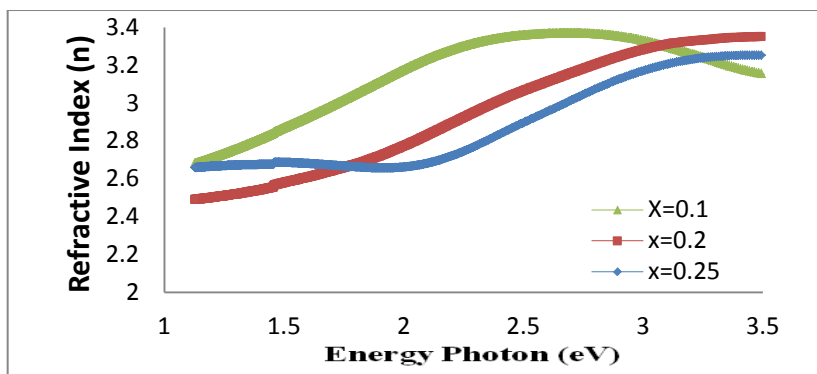

Fig.9: Refractive index behavior verses photon energy of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ films as a function of Cd content (x=0.1, 0.2 and 0.25)

It is clear from this figure that the refractive index values increases with increasing photon energy while it showed an opposite trend these values decreases with increase Cd content in films, this behavior may be due to change in the films structure after increase Cd content in films.

The dielectric constant was calculated using the relation[19]:

$\varepsilon = \varepsilon_1 - i\, \varepsilon_2$ ... (10)

Where : ε_1 , ε_2 are real and imaginary part of dielectric constant respectively and can be calculated from:

$\varepsilon_1 = n^2 - K^2 \qquad \dots (11)$

$\varepsilon_2 = 2nK \qquad \dots (12)$

The variation of the real (ε_1) and imaginary (ε_2) parts of the dielectric constant values as a function of photon energy for $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ thin films for (x=0.1, 0.2 and 0.25) is shown in figures (10),(11) respectively. From this figure we can deduce that the real part of the dielectric constant behavior nearly similar for all the range of the wavelength spectrum to that of the refractive index because of the real part depends mainly on refractive index according to the equation (11), while the imaginary part depend on the extinction coefficient values which are related to the variation of absorption coefficient, also we can see the values of the real part are higher than those of the imaginary part.
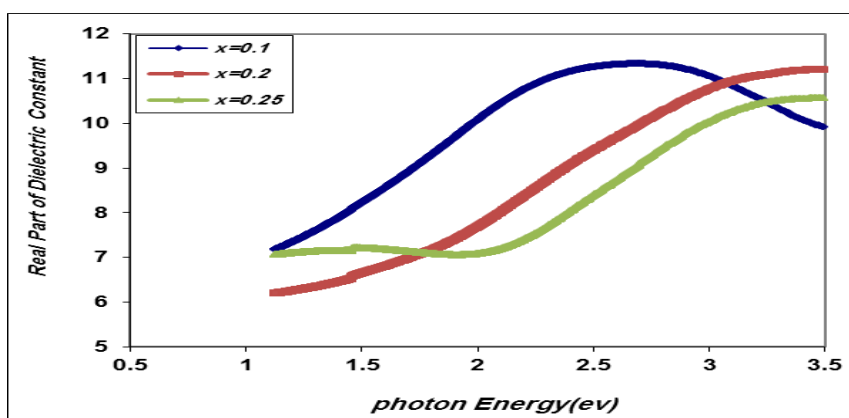

Fig.10: real part of dielectric constant behavior verses photon energy of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ films as a function of Cd content (x=0.1, 0.2 and 0.25)

Fig.(11): imaginary part of dielectric constant behavior verses photon energy of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ films as a function of Cd content (x=0.1, 0.2 and 0.25)

The optical conductivity (σ) was obtained using the formula[20]:

$$\sigma = \alpha \ nc \ / \ 4\pi \qquad ... (13)$$

Where (c) is the velocity of light.

 Fig. (12)   shows the variation of optical conductivity as a function of photon energy of $Hg_{1-x} Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ thin films for (x=0.1, 0.2 and 0.25), We can notice from this figure that the optical conductivity values increases with increasing photon energy while it decreases in general with increase Cd content in films. This behavior is due to the optical conductivity value depends mainly on refractive index and absorption coefficients according to the equation (13).
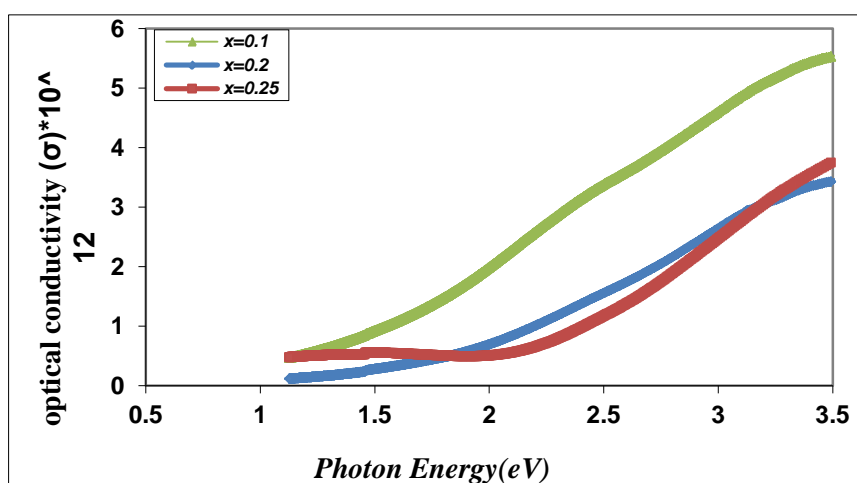

Fig. 12: Variation optical conductivity & photon energy for $Hg_{1-x} Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ films as a function of Cd content (x=0.1, 0.2 and 0.25)

CONCLUSION

The present study determines the influence of substitution cadmium Cd at the Hg site of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta.}$ superconductor with (x=0.1, 0.2 and 0.25) on the structural and optical properties of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ .thin films prepared by D.C sputtering technique. XRD pattern confirms all the samples have polycrystalline structure of multiphase formation tetragonal phase ,structural analysis results demonstrate that the formation of the Hg-2223 phase is difficult when the sample with small addition of Cd. (AFM) techniques indicate that the values of average size range decrease from (80,60 and 45) nm with increase Cd content (x=0.1, 0.2 and 0.25)   respectively. The optical properties of $Hg_{1-x}Cd_xBa_2Ca_2Cu_3O_{8+\delta}$ .thin films are seen to be dependent on the Cd concentration in films, and the values of all optical constant (absorption coefficient, refractive index, extinction coefficient, dielectric constant, and optical energy gap) affected after increase Cd ratio .

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