Growth of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ thin film Superconductors prepared by DC Sputtering

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Abstract

Structural and optical properties of Superconductors $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ with (x=0.0, 0.1 and 0.2) thin films prepared by DC sputtering technique on glass substrate at R.T (300) K with (150) nm thickness, have been studied.

XRD analyses of the samples showed polycrystalline of multiphase structure exhibited orthorhombic phase with lattice parameter and grain size changes when increase the Pb content percentage in the sample. The surface roughness average diameter, and Root Mean Square (RMS) of the films were estimated using topographical studies by (AFM) techniques.

The optical measurement within the wavelengths in the range (400-1100) nm showed that all films prepared have a direct optical energy gap, and it decrease with the increase Pb content while the optical constant such as absorption coefficient, refractive index, extinction coefficient, real and imaginary parts of the dielectric constant and optical conductivity showed an opposite trend, these values increase with the increase of Pb ratio in the sample.

Key words: thin films, Structural properties, Optical Constant, $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ Superconductors.

نمو اغشية رقيقة للمركب $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ فائق التوصيل والمحضرة بطريقة الترذيذ

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الخلاصة

تم دراسة الخواص التركيبية والبصرية للاغشية الرقيقة للمركب $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ فائق التوصيل ولقيم (x= 0.0,0.1,0.2) والمحضرة بطريقة الترذيذ على قواعد من الزجاج عند درجة حرارة الغرفة (300 K) بسمك (150 nm) . أظهرت فحوصات حيود الاشعة السينية (XRD) للنماذج

ان للمركب تركيب متعدد التبلور بطور معيني قائم ويتغير كل من ثوابت الشبيكة والحجم الحبيبي بزيادة نسبة محتوى Pb في النموذج .تم تشخيص خشونة السطح و معدل حجم الحبيبات و الجذر التربيعي لمربع متوسط الخشونة من خلال دراسة طوبوغرافية السطح بأستخدام تقنية مجهر القوة الذرية (AFM). اظهرت القياسات البصرية ضمن مدى الاطوال الموجية nm (400−1100) ان للاغشية المحضرة فجوة طاقة مباشرة تقل قيمتها بزيادة نسبة محتوى Pb في النموذج، بينما أظهرت الثوابت البصرية مثل معامل الامتصاص ومعامل الانكسار ومعامل الخمود وثابت العزل الكهربائي بنوعيه الحقيقي والخيالي والتوصيلية الضوئية سلوك معاكس أذ زادت قيمهم بزيادة نسبة Pb في النموذج .

الكلمات المفتاحية :− اغشية رقيقة ، الخصائص التركيبية، الثوابت البصرية ، Ba_{2-x} $Pb_xCa_2Cu_3O_{8+\delta}$ فائق التوصيل .

Introduction

$HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ represents the most interesting homologous series out of all known high temperatures superconductor compound (HTSC) [1, 2], which have the highest critical transition temperatures, Tc over (150) K under high pressure [3, 4]. $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ is one of the most promising materials for application in the modern microelectronics field[1,5].The other reason for Hg based (HTSC) phases being interesting is the fact that the anisotropy of these (HTSC) phases, due to show effective flux pinning and microstructure exhibiting good texturing of grains[1]. Unfortunately, there are still problems concerning the phase stability, because of their extreme sensitivity towards contamination from carbon dioxide and humidity[6-8].The understanding of normal state properties of oxide high temperature superconductors (HTSC) is essential since the formation of cooper-pairs sets[9], $HgBa_2Ca_2Cu_3O_{8+\delta}$ compound crystallizes as a result of converting of $HgCaO_2$ and $HgBa_2CaCu_2O_x$ phases through the intercalation process of Ba-Cu-O and Ca-Cu-O due to mixing level of the cations and strongly affects the formation rate of the Hg-1223 phase[5]. Several reports have been made to improve the stability of Hg-1223 phase and superconducting properties through suitable cationic substitutions for Hg [1-8].Many studies of doping into superconductor oxide ceramics have been made in order to improve their properties. Typically suited cations are those having oxidation states higher than that of Hg, which leading to phase stability and producing optimum critical transition temperature, such as Bi, Mo, Re, Sn, Pb, etc. [1,2,7]. A.Iyo et al [10] were found the $Ba_2\ Ca_{n-1}\ Cu_n\ O_{2n+2}$ compound consists of a mixture of phases (0223phase) at high Tc (120K), (0234 phase) at Tc=105 K and

(0212 phase) at low Tc (90 K). Several growth techniques have been used by different workers to prepare superconducting thin films, such as chemical vapor deposition, laser ablation, molecular beam epitaxy, co-evaporation , magnetron sputtering and the excimer laser etching[11] .In this work, we have successfully prepared superconducting $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ thin films with (x = 0.0, 0.1 and 0.2) by D.C. sputtering. Up to our knowledge no searches have been reported on synthesis $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ superconductor thin films. The influence of Pb substitution at Ba sites on the structural, topographical and optical properties of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ superconductor thin film are studied and analyzed.

Experimental

Two step processes is used for the synthesis $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ with ($0 \leq x \leq 0.2$) high critical temperature superconducting thin films. In the first step, mixed together weighed amount of pureed powdered materials BaO,Pb_2O_3,CaO and CuO in proportion to their molecular weights(Table 1) using an agate mortar for (24) hour. A sensitive balance whose sensitivity is of the order (10^{-4}) g was used to measure the weight of each material. A hydraulic press under a pressure of (6) ton/cm^2 was used to press the mixture into disc-shape pellets (5) cm in diameter and (0.2-0.3) cm thick. In the second step, thin films have been prepared on glass substrates from this mixture at R.T with thickness of (150) nm by using D.C. sputtering technique. Cathode voltage was ranging between (2-3) KV; 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 and the pellets were used as a target, the distance between the target and the substrates was about (4) cm, thin film have been obtained after running the system for (4) hours. Then annealed these films with exist air flow at temperature of (923) K for one hour by using (Kilns Furnaces).

The crystal structure properties of all prepared samples were observed by using X-ray diffraction (XRD) technique, which recording the intensity in the range of Bragg's angle θ from (20-80) using X-ray diffractometer system (SHIMADZU Japan XRD 600), source Cu K_α radiation of wavelength (λ=1.5405) A° was employed with generator setting of current (30) mA and voltage (40) KV. Atomic force microscope (AFM) technique was used to examine the surface morphology of these samples using SPM model AA3000 contact mode spectrometer, supplied by Angstrom Advanced Inc. Company, USA. A double beam spectrophotometer (UV/VIS) was used to determine the optical properties of these films by recorded the transmittance (T) and absorbance (A) spectrum in the range of wavelengths (400-1100) nm.

Results and Discussion

1-Structural Properties

According to the X-ray diffraction pattern of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ superconductor with critical transition temperatures (T_c)88, 92, and 97 K, respectively for ($0\leq x\leq 0.2$) films prepared by D.C. sputtering technique polycrystalline nature was obtained with orthorhombic phase formation, as shown in Fig.(1).It is clear from the figures mixed phases due to diffraction from different planes, H-Tc phase (0223), M-Tc phase (0234) and L-Tc phase (0212), in addition small concentrations of unknown phases. It is clear from this figure the variation in intensity and position of the peaks which indicating the change in phase composition and the lattice parameters of the samples. Using a computer program based on Cohen's least square method, the lattice constants (a), (b) and (c) can be calculated from the relation: [12]

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

Where (d) is the inter planer distance for different planes. The data of lattice parameters a, b, c/a and volume fraction of different phases are shown in Table (2). This Table indicates that a change in the structural parameters with random variation in both of a, b and c lattice constants with increasing Pb content.

The AFM has been used to see the effect of Pb content on the surface topography of $Ba2_{-x}Pb_xCa_2Cu_3O_{8+\delta}$ superconductor thin films where (x=0.0, 0.1 and 0.2). Fig.(2) shows the AFM images of these films for different Pb content in 2D and 3D which indicates the formation of grains packed very closely, hence revealing the crystalline nature. However, the surface topography of these films exhibit the grains are uniformly distributed features with no pinholes or island structure. The values of average diameter, average surface roughness and Root Mean Square (RMS) are listed in the Table (3)

2-Optical Properties

Fig. (3) Shows the influence of different Pb content on the absorbance (A) of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ superconductor with (x=0.0, 0.1 and 0.2) thin films within the wavelength range (400 – 1100) nm. From this figure it can be noticed that the films have high absorption at (400-500)nm and the absorbance values decreased with the increasing of wavelength while it increased with increasing the Pb content in the sample for all values of the wavelength due to the fact that the absorption is not attributed to the free carriers only, but to impurities or localized electronic states ; Pb introduces inter band energy levels in the band gap of these films which make a stronger interaction among them , this can be attributed to the change in the films structure which leads to increase the absorbance values.

Fig.4 shows the plots of transmittance (T) as a function of wavelength for $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ superconductor with (x=0.0, 0.1 and 0.2) thin films which calculated from the relation: [12]

$$T = 10^{-(A)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

It is clear from this figure that the transmittance values increase generally as the wavelength increases and have high values in the NIR region; all samples demonstrate (45-95) % transmittance which makes these films suitable for solar cell window. The maximum value of optical transmittance is about 95% in the wavelength range (700-1100) nm recorded for the film with (x=0.0).

The values of incident photon energy (E=hν) are calculated as a function of wavelength (λ) using equation: [13]

$$E\,(eV) = 1240 / \lambda\,(nm) \ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

The variation of absorption coefficient with the wavelength of the incident photon energy was calculated according to equation: [13]

$$\alpha = 2.303\,(A / t) \ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(4)}$$

Where (t) is film thickness.

Fig.(5) illustrates the variation of absorption coefficient (α) as a function of photon energy for $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ superconductor with (x=0.0, 0.1 and 0.2) thin films, it is observed from this figure that all the films have high values of absorption coefficient ($\alpha > 10^4\ cm^{-1}$) this means that the direct transition possibly occurs also we can notice from this figure that the absorption coefficient values increased with the increasing of Pb content and photon energy within the whole range of the spectrum. This behavior may be due to the change in crystal structure of these films with increase Pb content for the same reasons as we mentioned before.

The optical energy gap (Eg^{opt}) values for $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ superconductor with (x=0.0, 0.1 and 0.2) thin films have been determined by using Tauc equation: [14]

$$(\alpha h\nu) = B`\,(h\nu - Eg^{opt})^{r} \ldots\ldots\ldots\ldots\ldots\ldots \text{(5)}$$

Where B` is a constant inversely proportional to amorphousity, r is constant depending on the type of the optical transition. The allowed direct transition is determined by plotting $(\alpha h\nu)^2$ versus photon energy (hν) and selecting the optimum linear part, (Eg^{opt}) is determined by the extrapolation of the linear portion at (α hν =0) as shown in Fig.6.

It is clear from this figure that the optical energy gap values decrease, were found to be (2.7, 2.3 and 2.1) eV when the Pb content increased in films for (x=0.0, 0.1 and 0.2) respectively. This is due to the generate extra energy levels between the valance and conduction bands.

The values of the refractive index (n) are calculated using equation: [15]

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

Depending on the reflectance (R) and extinction coefficient (k), the reflectance (R) can be calculated using equation: [15]

$$R = 1\text{-}T\text{-}A \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

While the extinction coefficient (k) can calculated using equation: [14]

$$k = \alpha \lambda / 4\pi \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

The complex dielectric constant can be introduced by: [16]

$$\varepsilon = \varepsilon_1 \text{-} i\, \varepsilon_2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Where $\varepsilon_1 = n^2 \text{-} k^2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$

$$\varepsilon_2 = 2nk \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Where ε_1= real part of dielectric constant, ε_2 = imaginary part of dielectric constant.

Figures from (7) to (10) show the variation of these optical constants (n, k, ε_1, and ε_2) respectively as a function of photon energy for $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ superconductor with (x=0.0, 0.1 and 0.2) thin films. It is clear from these figures that all optical constants increased with the increasing Pb content in films for the same reasons as we mentioned before.

The optical conductivity (σ) was calculated using the relation: [17]

$$\sigma = \alpha nc / 4\pi \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

Where (c) is the velocity of light.

Fig.(11) shows the variation of optical conductivity with photon energy of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ superconductor with (x=0.0, 0.1 and 0.2) thin films .This figure shows that the optical conductivity value increases with increasing photon energy and with increase Pb content in films. This behavior is due to the optical conductivity value depends mainly on refractive index and absorption coefficient according to the equation (12).

Conclusion

Thin films of $Ba2_{-x}Pb_xCa_2Cu_3O_{8+\delta}$ superconductor with (x=0.0, 0.1 and 0.2) were deposited on glass substrate using D.C. sputtering technique. XRD analysis reveals that deposited films are exhibit polycrystalline of multiphase formation with orthorhombic phase. The structural parameters such as lattice parameters a, b, c/a and volume fraction of different phases are evaluated and their values change with addition Pb to samples. AFM measurements shows that the grains are uniformly distributed features with no pinholes or island. The optical transitions in these films are direct and the values of optical energy gap and the transmittance decreased with increasing the Pb content in films while the absorbance values increase after addition Pb.The transmittance values of these films are high in the NIR region (700-1100) nm, which makes it suitable for use as a window material in photovoltaic application. According to the optical results, all optical constant (refractive index, absorption coefficient, extinction coefficient, real and imaginary parts of the dielectric constant and optical conductivity) are increasing with increase of the Pb content in the samples.

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Table (1): Weighed amount of pure powders materials BaO, Pb_2O_3, CaO and CuO in proportion to their molecular weights

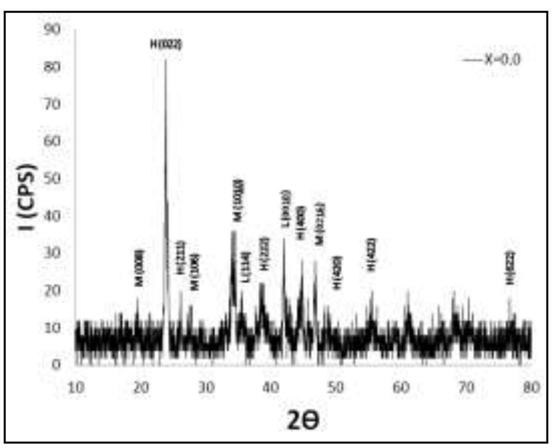
0.2≥x≥0	**$Ba_{(2-x)}$ Pb_x Ca_2Cu_3**
(2-x) BaO	(2-x)(137.33+15.999)
x Pb_2O_3	x ((2×207.2006)+3×15.9994))
CaO	2× (40.078+15.999)
CuO	3× (63.546+15.999)

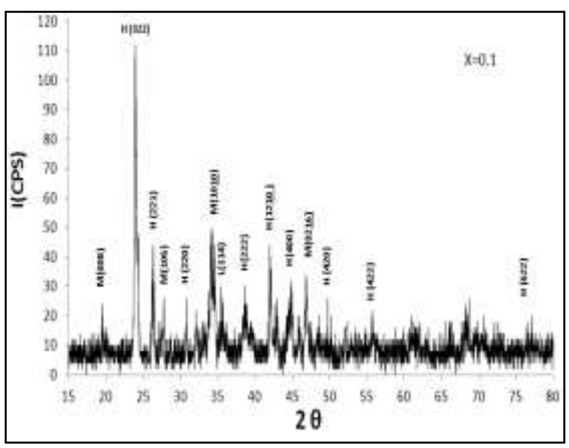
Table (2): Lattice parameter and volume fraction of phases for $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ with (x=0.0, 0.1 and 0.2) thin films.

x	**a(Å)**	**b Å**	**c Å**	**c/a**	**H Vph%**	**M Vph%**	**L Vph%**
0.0	4.051	4.136	20.101	4.961	56.98006	27.63533	15.38462
0.1	8.478	6.214	21.09	2.487	73.02905	20.74689	6.224066
0.2	4.680	4.071	21.067	4.501	78.83916	15.78322	5.37762

Table (3): AFM results of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ with (x=0.0, 0.1 and 0.2) thin films

x	**Average diameter (nm)**	**Average roughness (nm)**	**RMS (nm)**
0.0	85.72	0.204	0.249
0.1	96.18	0.471	0.598
0.2	85.22	0.0995	0.126





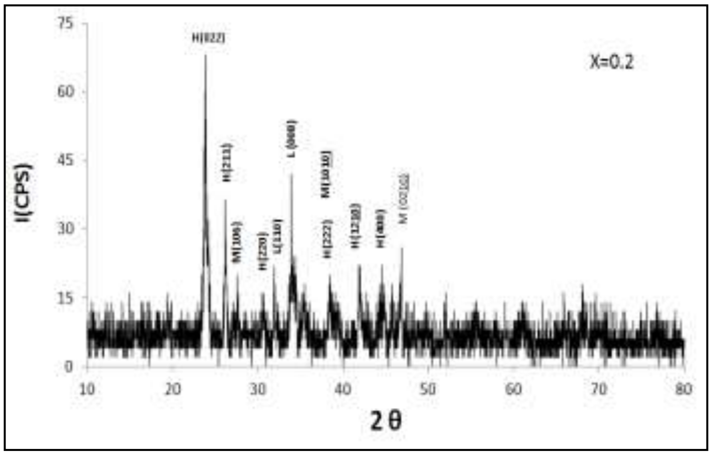


Fig. (1): X-ray diffraction pattern of of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ thin films with different Pb content (x=0.0, 0.1 and 0.2)

(a)

(b)

(c)

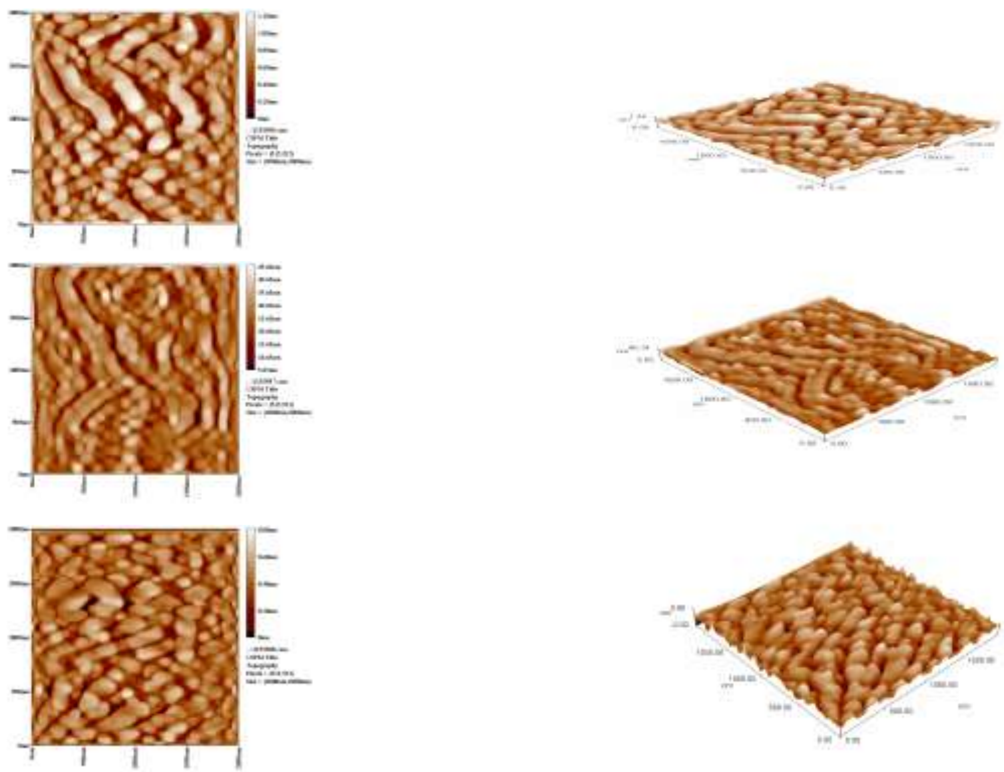


Fig. (2): 2D &3D AFM images of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ thin films with different Pb content (a) x=0.0; (b) x=0.1; (c) x=0.2

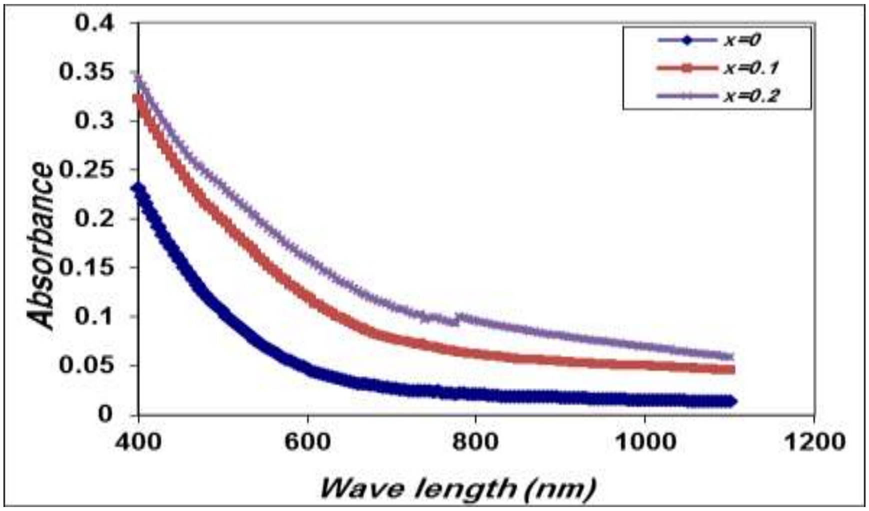


Fig. (3): Variation of absorbance versus wavelength of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ thin films with different Pb content (x=0.0, 0.1 and 0.2).

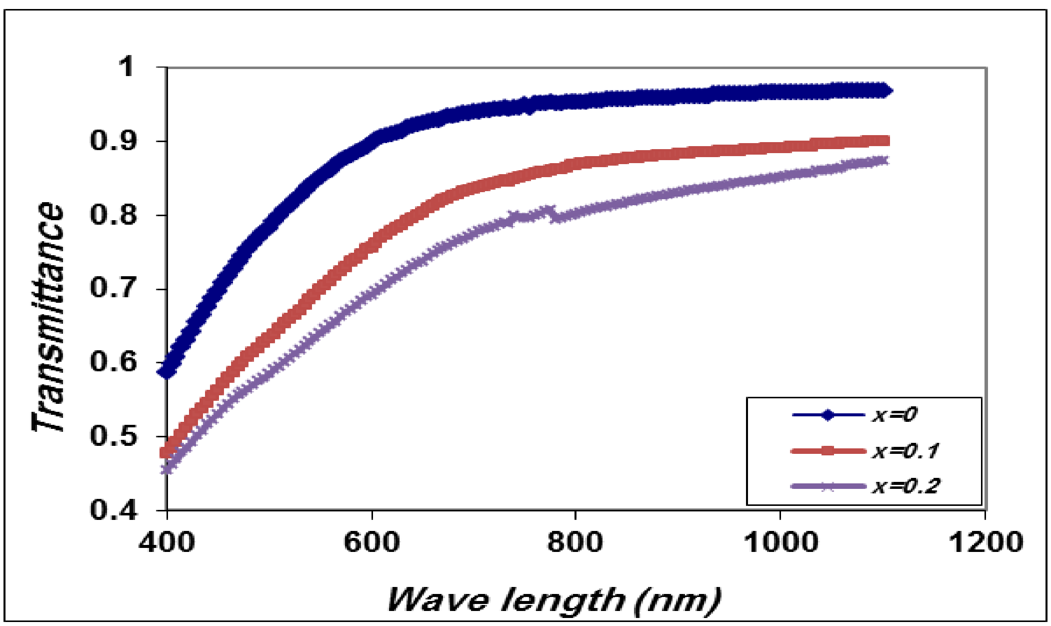


Fig.(4): Variation of transmittance versus wavelength of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ thin films with different Pb content (x=0.0, 0.1 and 0.2).

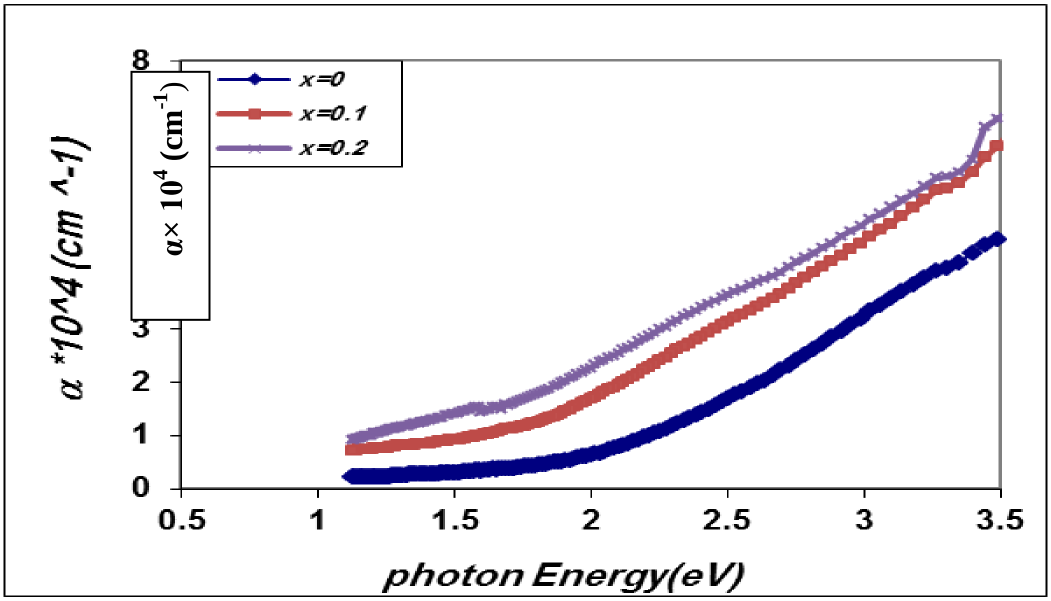


Fig. (5): Absorption coefficient versus photon energy of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ thin films with different Pb content (x=0.0, 0.1 and 0.2).

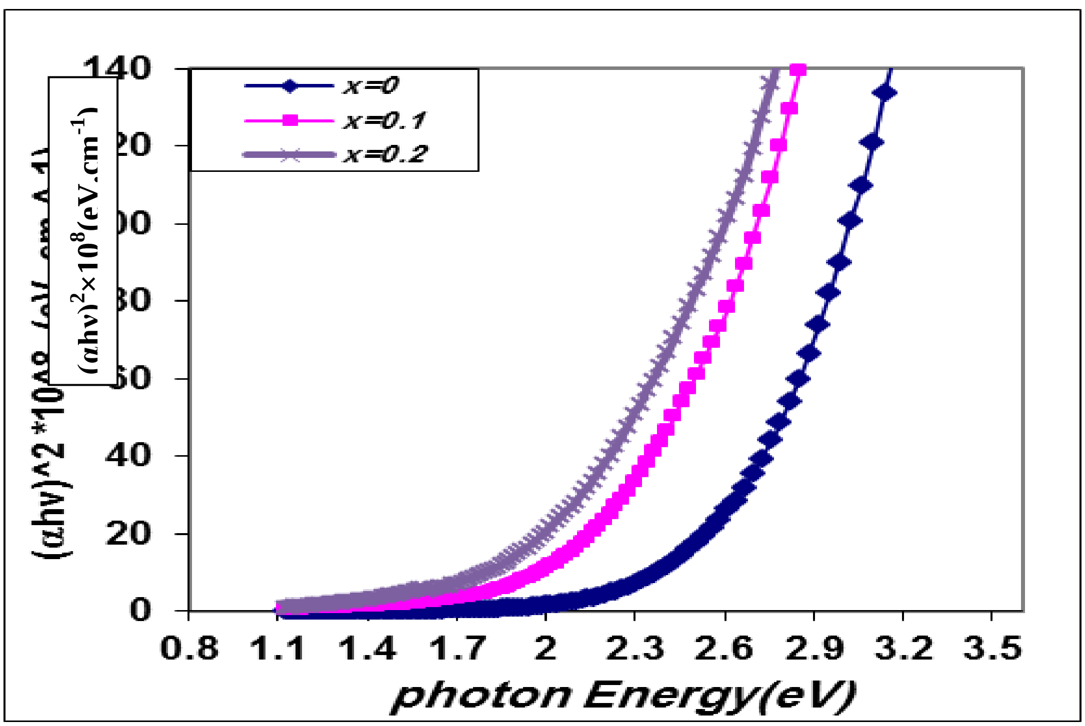


Fig. (٦): Variation of $(\alpha\, h\nu)^2$ versus photon energy of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ thin films with different Pb content (x=0.0, 0.1 and 0.2).

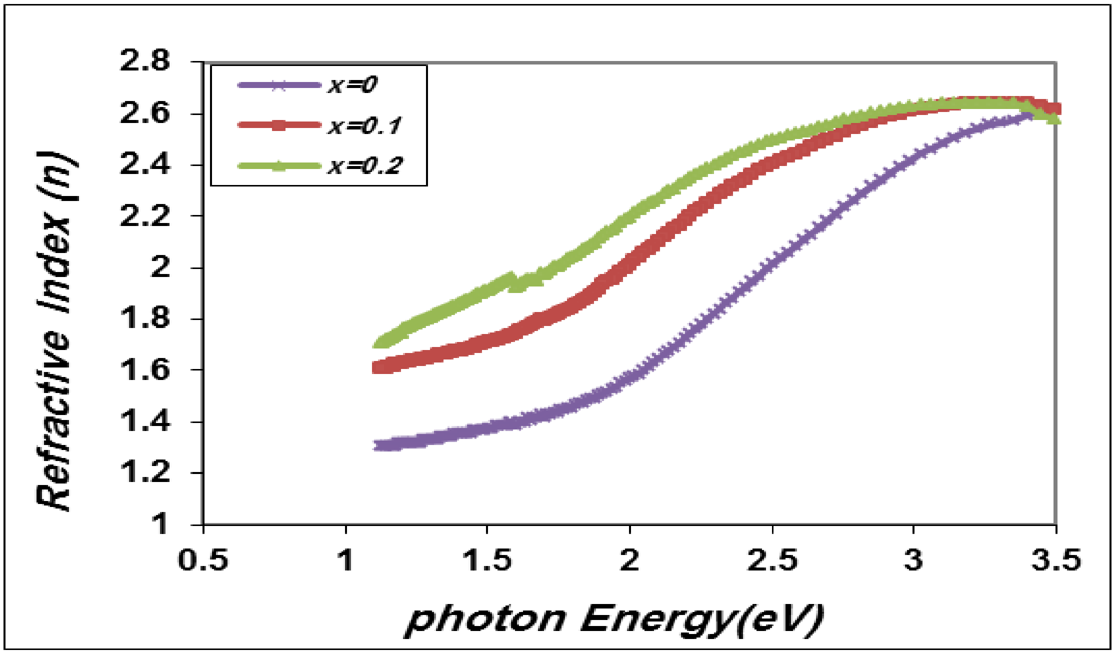


Fig. (7): Variation of refractive index versus photon energy of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ thin films with different Pb content (x=0.0, 0.1 and 0.2).

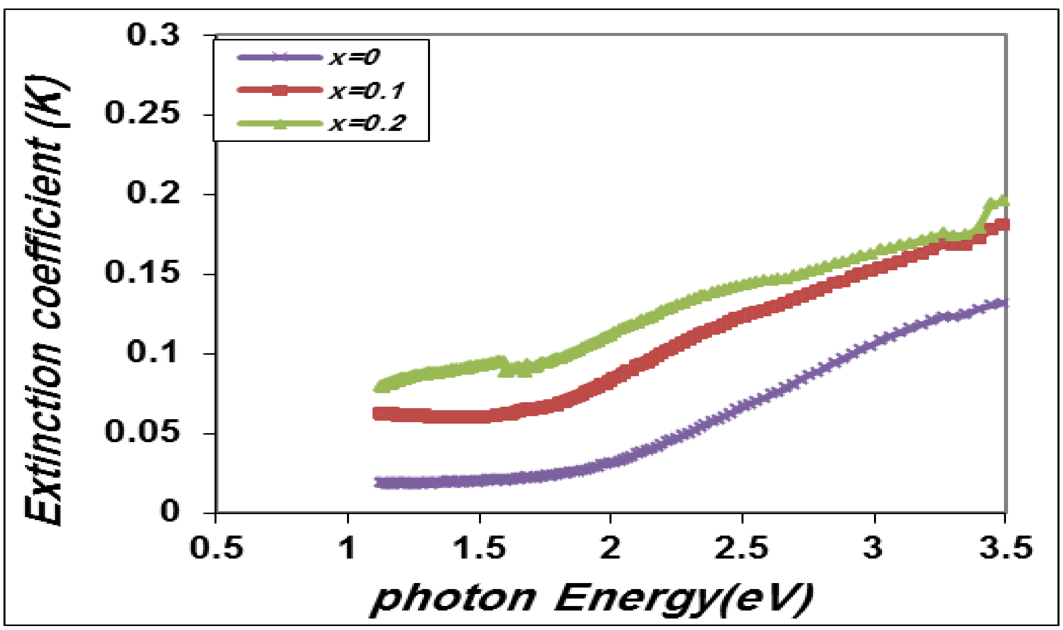


Fig. (8): Variation of extinction coefficient versus photon energy of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ thin films with different Pb content (x=0.0, 0.1 and 0.2).

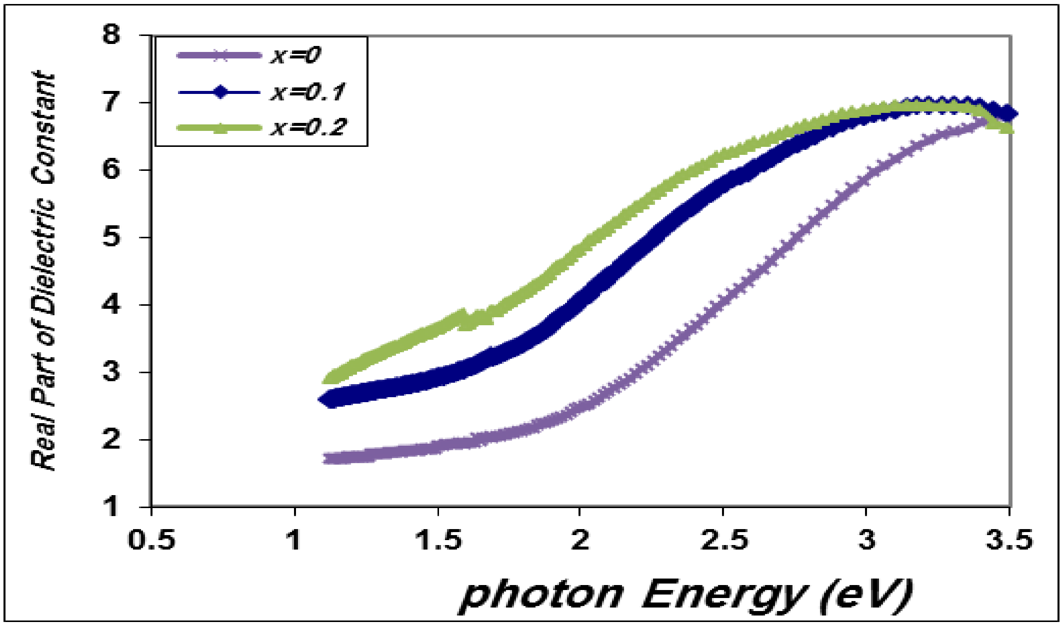


Fig. (9): Variation of Real part of dielectric constant versus photon energy of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ thin films with different Pb content (x=0.0, 0.1 and 0.2).

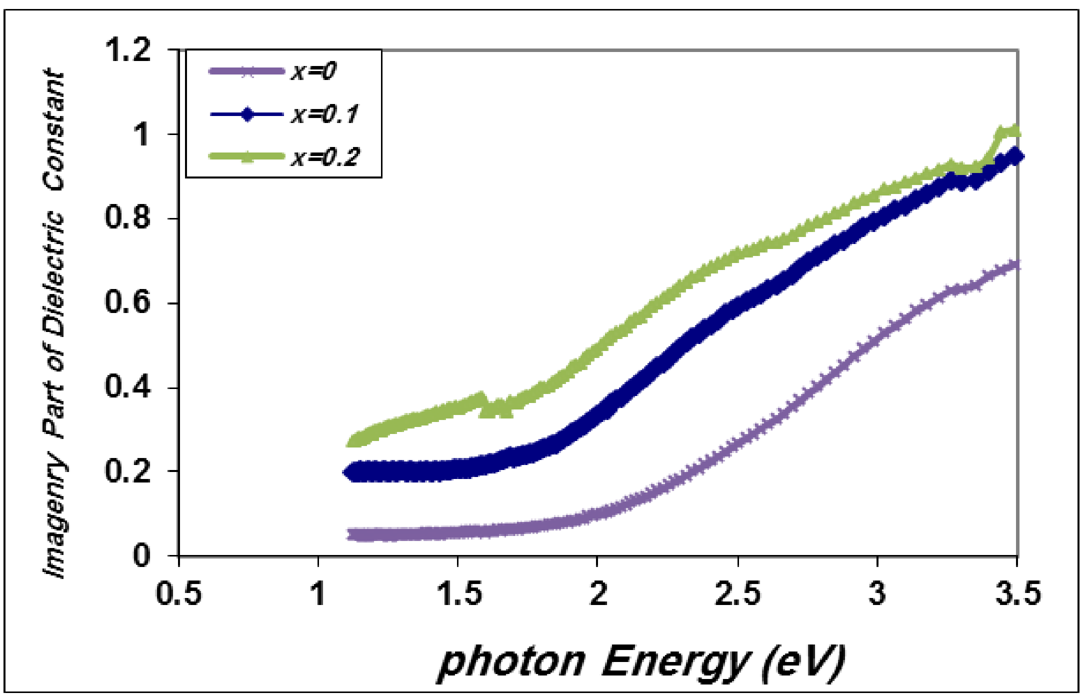


Fig. (10): Variation of Imaginary part of dielectric constant versus photon energy of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ thin films with different Pb content (x=0.0, 0.1 and 0.2).

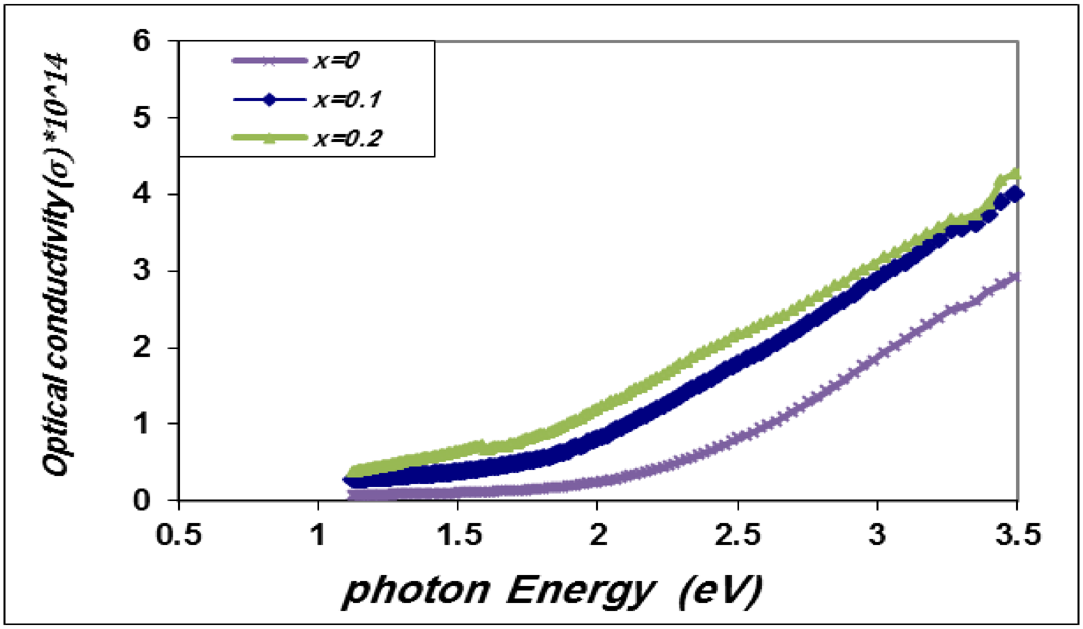


Fig. (11): Optical conductivity versus photon energy of $Ba_{2-x}Pb_xCa_2Cu_3O_{8+\delta}$ thin films with different Pb content (x=0.0, 0.1 and 0.2).