# Structural variations induced by difference of optical properties of thin films (Bismuthinite-Guanajuatite) $Bi_2S_{3x}Se_{3(1-x)}$

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## Abstract

Thin films from bismuthinite $Bi_2S_3$ and guanajuatite $Bi_2Se_3$ and their mixture $Bi_2S_{3x}Se_{3(1-x)}$ were prepared by vacuum evaporation under low vacuum ($10^{-5}$ torr) on clean glass substrates at 300 $^oK$. X-ray diffractions are studied to show that all films as-deposited have been amorphous structure and become polycrystalline after annealing at 533 $^oK$. They have rhombohedral structure at compositions (x=0.0,0.2,0.4,0.6) and orthorhombic structure at (x=0.8,1.0). Optical properties are studied includes determinations of absorption coefficient from the absorbance, transmittance spectrum range (300-900)nm and estimation of energy gaps before and after annealing which was (1.75-1.84) eV and (1.74-1.7) eV respectively and their mixture is about between these values.

### 1- Introduction:

Binary semiconductor compounds from the group $V_2$-$VI_3$ have bismuthinite $Bi_2S_3$ and guanajuatite $Bi_2Se_3$ structure which contains bismuth element with sulfur and selenium elements respectively and have space group Pnma-$D_{2h}^{16}$ (P. Arun et al. 1999). The bonding scheme of these compounds allows a direct determination of the position of atomic plane consisting of either Bi or Se (Bi or S) hexagonally arranged atoms are stacked in a closed packing fcc fashion; 5 atomic planes with atomic order Se1-Bi-$Se_2$-Bi-Se1, (S1-Bi-$S_2$-Bi-S1) for layers as shown in Figure (1) (S. Urazhdin et al. 2002).

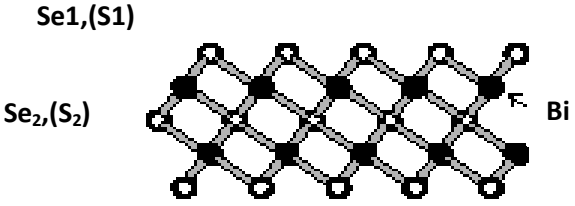


**Figure Se1(3),(S1(3))(1) Structure $Bi_2Se_3$, ($Bi_2S_3$)**

**showing atomic order in a layer**

The atoms S and Se are called chalcogenide (S,Se,Te and Pe) atoms which that donor one electron to mineral atom to form anion and all mineral atoms accept three electrons to form cation (M.Stolzer et al.1997). The stoichiometric as grown $Bi_2Se_3$ samples are n-type with carrier concentration of about $10^{19}$ $cm^{-3}$. Doping samples with excess Bi introduces substitutional Bi defects at Se sites ($Bi_{Se}$ antisites) which are shallow acceptors. However, because of the low solubility of Bi, the Bi doped is n-type due to the compensating defect and its doping with excess Se introduces shallow donor-type Se substitutional defects at the Bi sites ($Se_{Bi}$ antisites) (M. Stolzer et al. 1997). The absorption of many semiconductors materials has been observed to obey the equation(Jai Singh 2006):

$$\alpha h\nu = A(h\nu - E^{Opt.})^r \qquad (1)$$

Where (α) is the absorption coefficient, $E^{Opt.}$ is the optical energy gap, A is a constant and r an index which can be assumed to have values of 1/2, 3/2, 2 and 3 depending on the nature of the electronic transition responsible for the absorption.

The optical constants such that refractive index (n), real($\varepsilon_r$ ) and imaginary ( $\varepsilon_i$ ) dielectric constant can be related to the wavelength by the following equation (W.R.Rumgon 1975):

$$n = \left( \frac{4R}{(R-1)^2} - k^2 \right)^{1/2} - \frac{(R+1)}{(R-1)} \qquad (2)$$

Where R is the reflectance which is obtained by the following equation (D. Eya 2005):

$$T = (1-R)^2 \exp(-\alpha t) \qquad (3)$$

Where T is t he transmtance, and t is the thickness of thin film.

The dielectric constant can be determined by the following (Jai Singh 2006):

$$\varepsilon_r = n^2 - k^2 \qquad (4)$$

$$\varepsilon_i = 2nk \qquad (5)$$

Where k is the extinction coefficient.

The optical conductivity σ is (Ezema et al. 2003):

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

This work deals with the optical processes that occur for photons having energies comparable to that of the band gap in $Bi_2S_{3x}Se_{3(1-x)}$ thin films.

**2-Experimental:**

The thin films from $Bi_2S_3$ and $Bi_2Se_3$ compounds and their mixture $Bi_2S_{3x}Se_{3(1-x)}$ (x=0.0,0.2,…..,1) were prepared using a fast thermal evaporation technique from titanium boat by Varian 3117 system under low vacuum pressure $10^{-5}$ torr on clean glass substrates at 300 $^oK$ and several thickness. Annealing process were carried under rotary pressure $10^{-2}$ torr at 533 $^oK$ for one hour only. Thin films were studied by x-

ray diffraction (Philips model 3055). Optical properties studying for as-deposited and annealed films from the absorbance and transmittance spectral have been recorded using single beam UV-VIS spectrophotometer at wavelength between (300-900)nm.

**3-Results and discussion:**

XRD patterns of the $Bi_2S_{3x}Se_{(1-x)}$films at 533 $^oK$ are shown in Fig.(2). It was shown that the crystallinity of $Bi_2S_{2.4}Se_{0.6}$films is better than that of the other films.It was concluded from this result that the crystallinities of films were spoiled with S concentration. It was determined that the preferntial orientation of $Bi_2S_{2.4}Se_{0.6}$ film is (310). The preferential orientation changed with S concentaration. Table(1) shows the variation of system structure from rhombohedral stucture at x=0.0,0.2,0.4,0.6 to orthohombic stucture at x=0.8,1.0,and the lattice constant of $Bi_2S_{3x}Se_{3(1-x)}$ thin films compound. The atomic levels in crystal structure and the lattice constant a,b,and c of films were calculated according to the following equations(B.Cullity 1967):

$$2d_{hkl}\,\mathrm{Sin}\theta=n\lambda \qquad (8)$$

$$\frac{1}{d^2}=\frac{\left(h^2+k^2+l^2\right)\sin^2\alpha+2\left(hk+kl+hl\right)\left(\cos^2\alpha-\cos\alpha\right)}{a^2\left(1-3\cos^2\alpha+2\cos^3\alpha\right)} \qquad (9)\text{for rhomb. system}$$

,and, $$\frac{1}{d^2}=\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2} \qquad (10)\text{ for orthor. System}$$

In the high photon energy region ;the energy dependence of the absorption coefficient, ($\alpha > 10^5$ $cm^{-1}$ ) suggests the occurrence of direct optical transition as shown in Fig (3). Since the absorption coefficient ($\alpha$ ) for the allowed direct inter band transition in a crystal is proportional to $(h\upsilon)^{-1}(h\upsilon\text{-}E_g)^{1/2}$ for $h\upsilon \geq E_g$, where $h\upsilon$ is the photon energy end $E_g$ is the value of the energy gap, we can estimate $E_g$ by plotting $(h\upsilon\,\alpha)^2$ as a function of $h\upsilon$( K.Yamaguchi.1984 ) as shown in Fig(4). It can be seen from table (2) that the energy gaps are increasing with S concentration. The films composition X was determined from the band gap dependence on the deposition in the $Bi_2S_{3X}Se_{3(1-x)}$ system ( D.Bonnet.1972). Fig (5) shows the variation of refractive index (n) of $Bi_2S_{3X}Se_{3(1-x)}$ with $h\upsilon$. The films annealed at higher temperature, especially those annealed at 533 $^oK$, show that the refractive index remained, constant at both visible and NIR regions. Reflectance (R) as a function of $h\upsilon$ are shown in Fig (6). The films annealed at 533 $^oK$ have reflectance of 20% on the average in all region of the spectrum i.e. the reflectance of the films at 533 $^oK$ almost increased with $h\upsilon$. Variation of the extinction coefficient (k) with $h\upsilon$ are shown in Fig (7). For films annealed at 533 $^oK$ there is a steep linear relationship indicating sharp decreases in the absorption with $h\upsilon$ (Ezema et al . 2003). Real part ($\varepsilon_r$) and imaginary ($\varepsilon_i$) of dielectric constant as a function of $h\upsilon$ of $Bi_2S_{3X}Se_{3(1-x)}$ thin films are shown in Fig (8) and (9) respectively. One can observe that the variation of ($\varepsilon_r$) is similar to that of (n) as shown in equation (4), while the variation of (

$\varepsilon_i$) depends on the variation of (k) as shown in equation (5). Finally Fig (10) shows the variation of optical conductivity of $Bi_2S_{3X}Se_{3(1-x)}$ with $h\upsilon$, where the optical conductivity increased with increasing $h\upsilon$ and represents the alternative conductivity in which that the power losing at alternative field is due to the insulators and semiconductor ( W.Weber et. Al. 2003).

**4-Conclusion:**

$Bi_2X_3$; (X= S, Se) films and their mixture have been successfully prepared by thermal evaporation under low pressure $10^{-5}$ torr at 300 $^oK$ which have amorphous structure. After annealing at 533 $^oK$ they have polycrystalline structure. By different compositions we obtained that two systems which are rhombohedral and orthorhombic systems. On average, $Bi_2S_{3X}Se_{3(1-x)}$ shows reflectance of 20% in all regions of the electromagnetic spectrum. It also shows reflectance index of 2.6

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**Table (1) Shows the variation of system structure and lattice constant of $Bi_2S_{3x}Se_{3(1-x)}$ thin films compound.**

| x | a Å | b Å | c Å | system |
|---|---|---|---|---|
| 0.0 | 3.603 | - | 29.076 | Rhombo. |
| 0.2 | 13.271 | - | 28.602 | Rhombo. |
| 0.4 | 13.177 | - | 28.915 | Rhombo. |
| 0.6 | 13.141 | - | 28.637 | Rhombo. |
| 0.8 | 11.004 | 11.443 | 3.235 | Orthor. |
| 1.0 | 11.107 | 11.614 | 3.230 | Orthor. |

**Table (2) Shows the optical band gap a-deposited and annealed at 533 $^oK$ of $Bi_2S_{3x}Se_{3(1-x)}$ thin films compound.**

| x | $E_g$ (eV) at 300 $^oK$ | $E_g$ (eV) at annealed 533 $^oK$ |
|---|---|---|
| 0.0 | 1.75 | 1.74 |
| 0.2 | 1.79 | 1.73 |
| 0.4 | 1.8 | 1.6 |
| 0.6 | 1.9 | 1.55 |
| 0.8 | 1.7 | 1.55 |
| 1.0 | 1.84 | 1.7 |

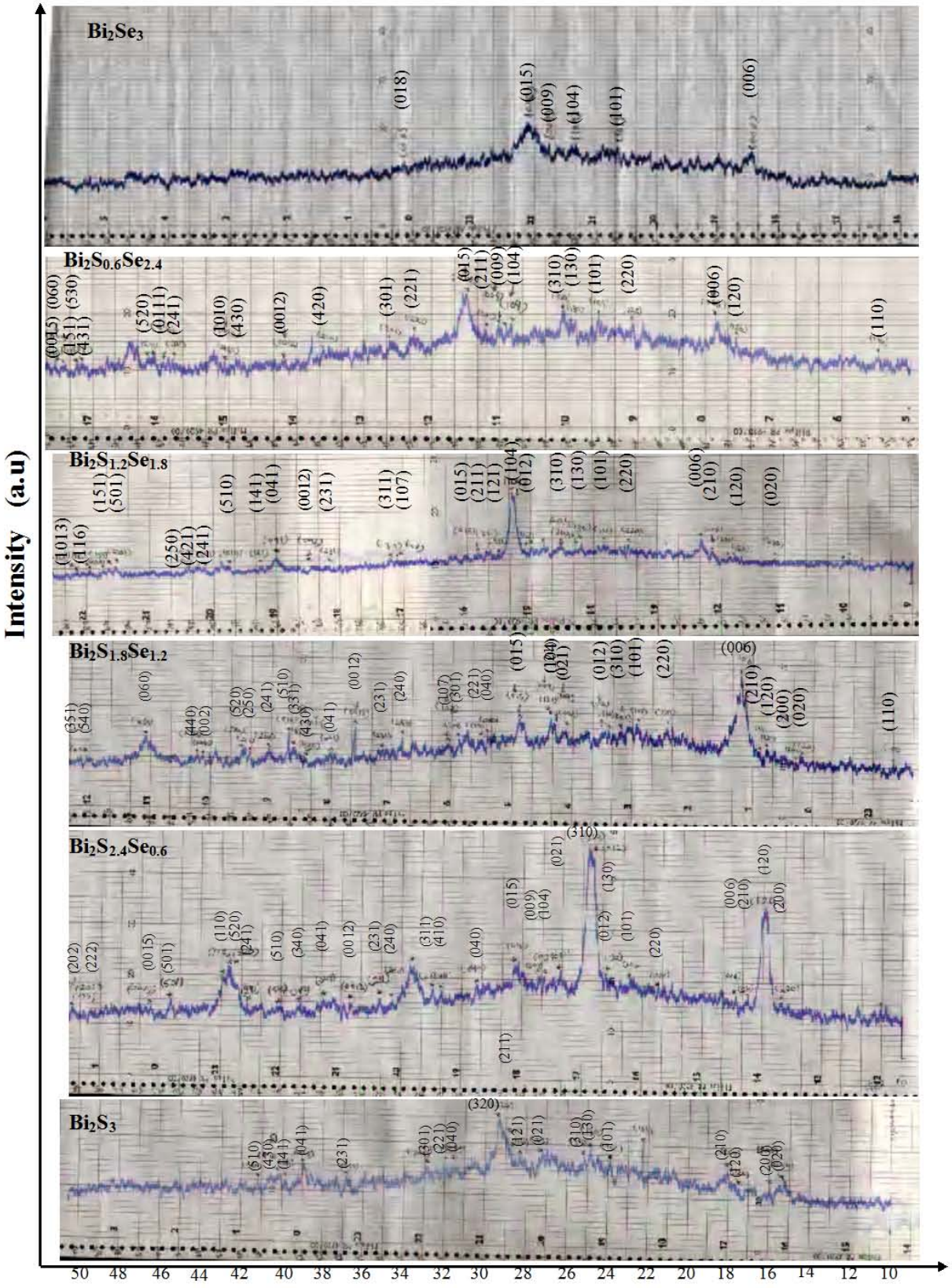


**Figure (2) Shows the X-ray diffraction pattern of annealing $Bi_2S_{3x}Se_{3(x-1)}$ thin films at 533 $^oK$.**

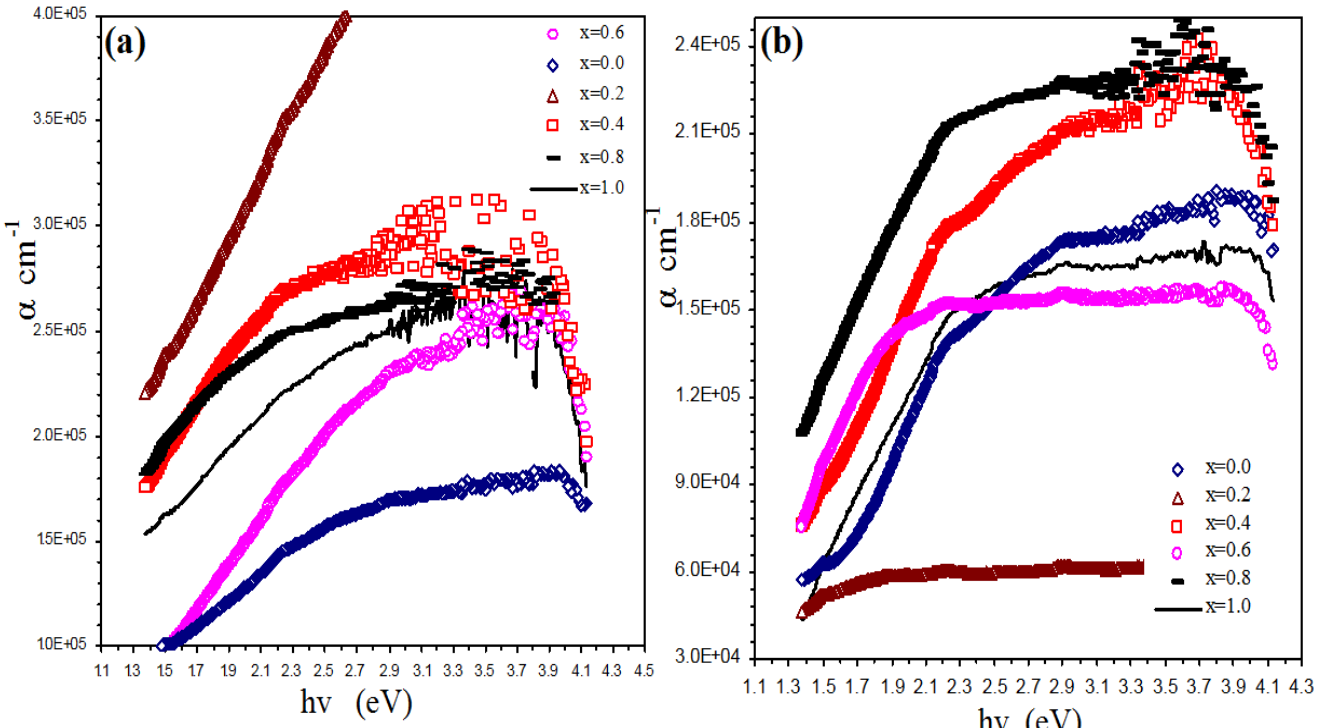


Figure (3) Shows the absorption coefficient versus photon energy of thin films $Bi_2S_{3x}Se_{3(1-x)}$ compound at a-300 $^{o}$K and b-533 $^{o}$K .

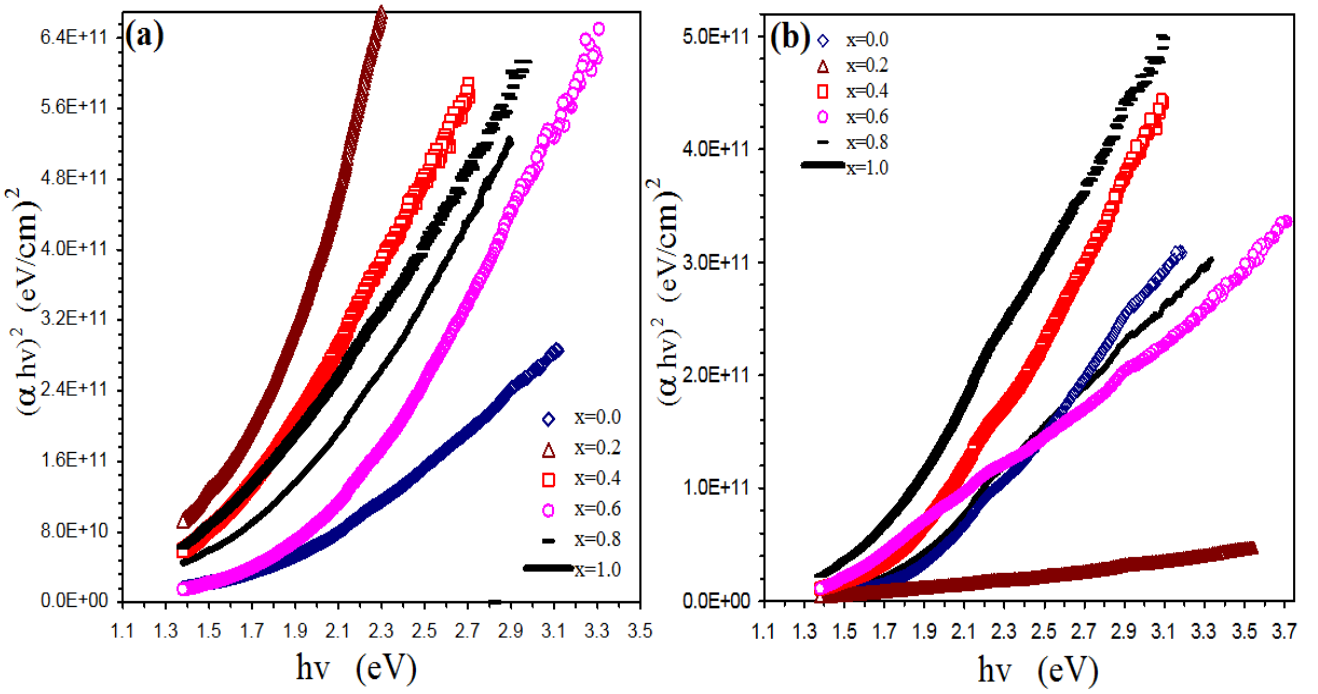


Figure (4) Shows the $(\alpha hv)^2$ versus photon energy of thin films $Bi_2S_{3x}Se_{3(1-x)}$ compound at a-300 $^{o}$K and b-533 $^{o}$K.

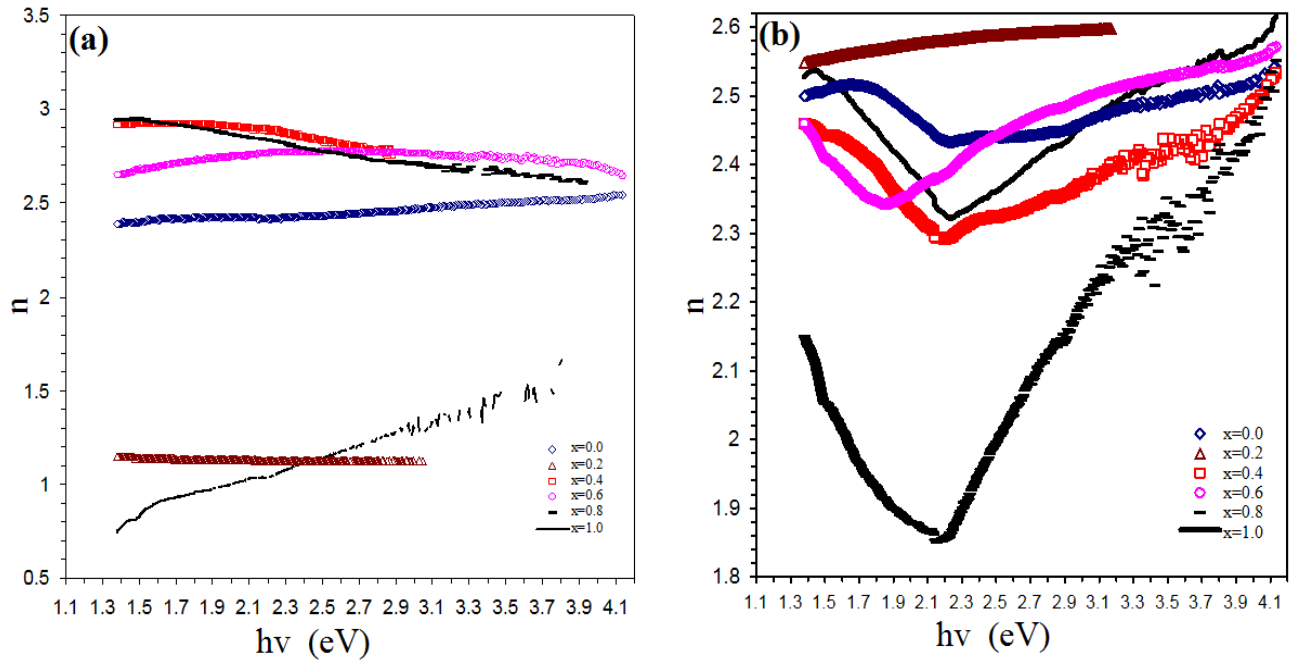


Figure (5) Shows the refractive index versus photon energy of thin films $Bi_2S_{3x}Se_{3(1-x)}$ compound at a-300 $^{o}$K and b-533 $^{o}$K.

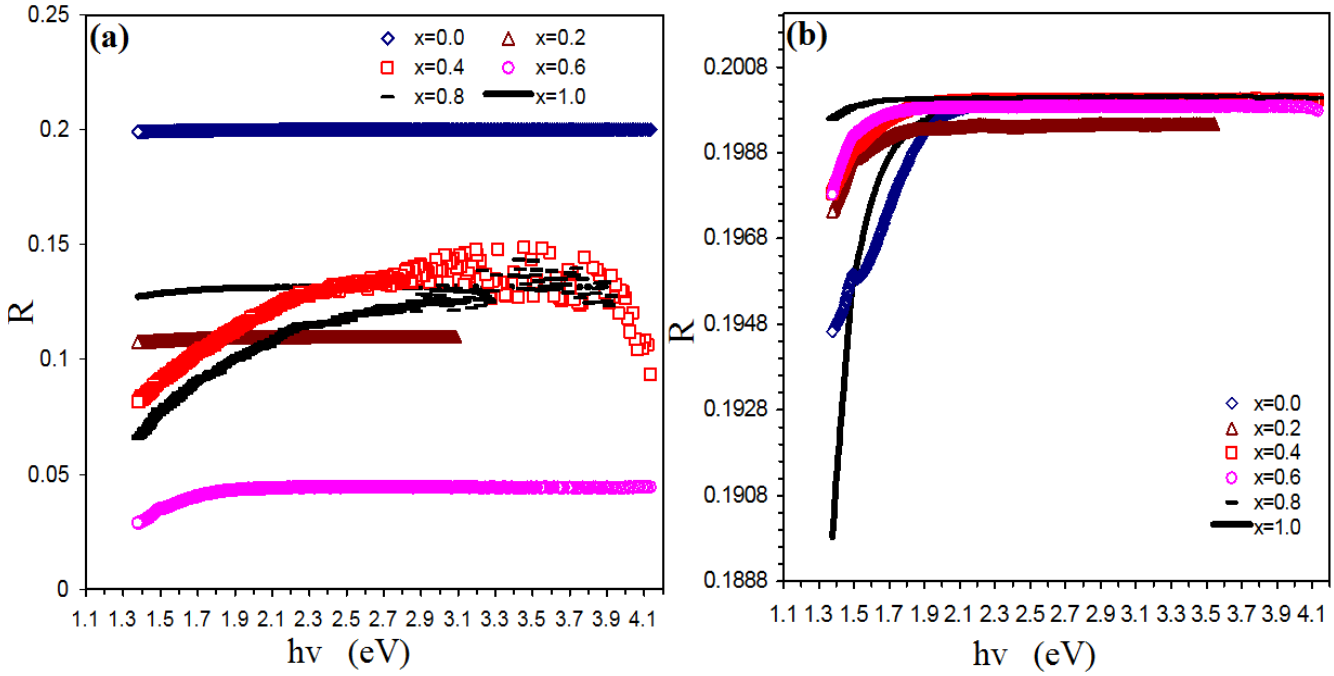


Figure (6) Shows the reflectivity spectra versus photon energy of thin films $Bi_2S_{3x}Se_{3(1-x)}$ compound at a-300 $^{o}$K andaz b-533 $^{o}$K.

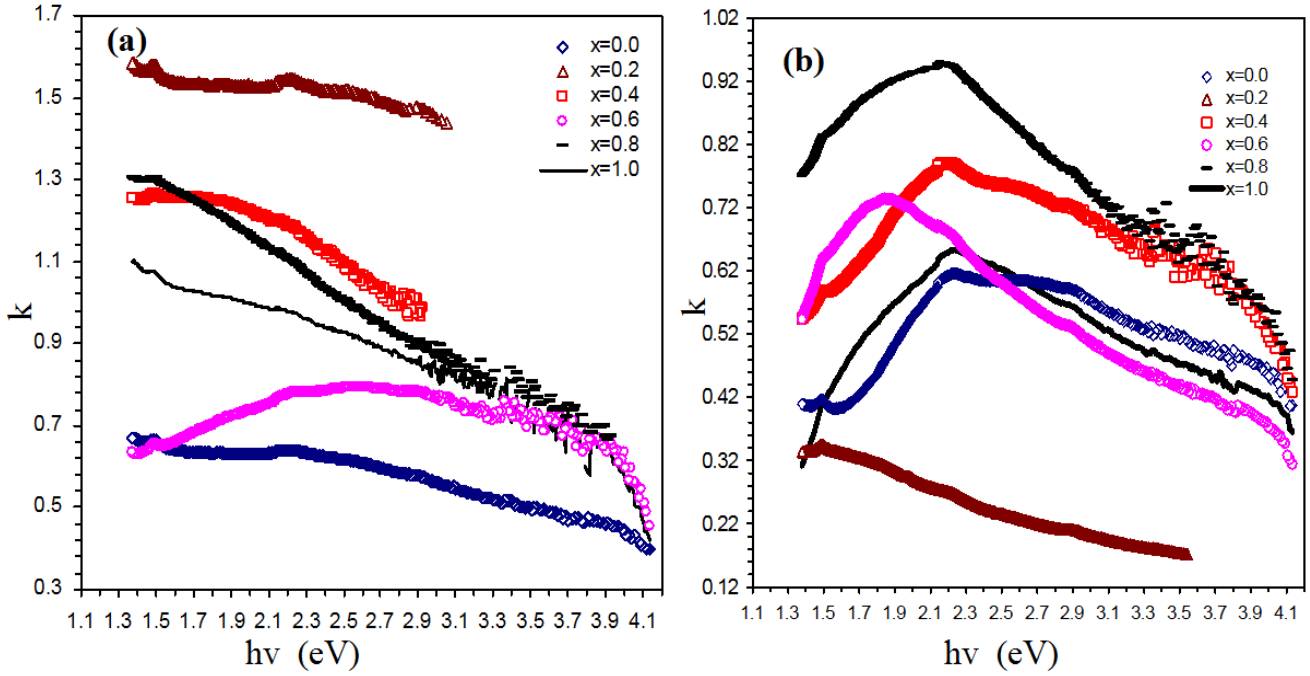


Figure (7) Shows the exaction coefficient versus the photon energy of thin film $Bi_2S_{3x}Se_{3(1-x)}$ compound at a-300 $^oK$ and b-533 $^oK$.

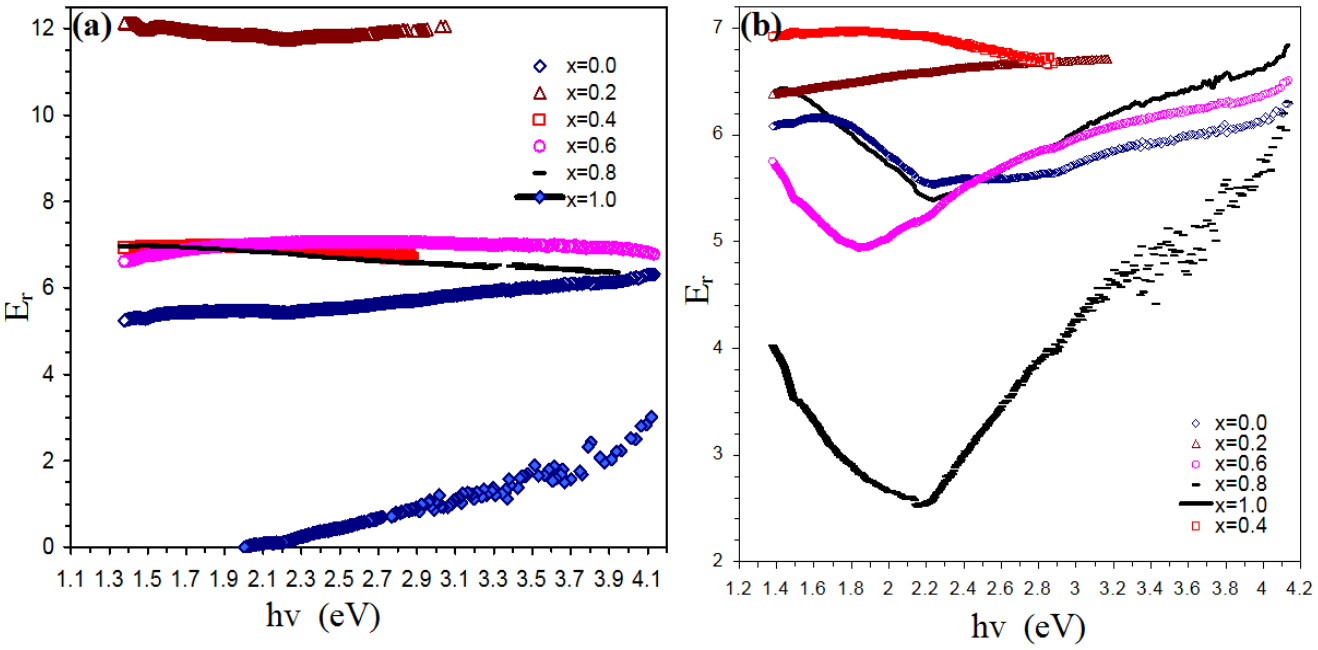


Figure (8) Shows the real dielectric constant versus photon energy of thin films $Bi_2S_{3x}Se_{3(1-x)}$ compound at a-300 $^oK$ and b-533 $^oK$.

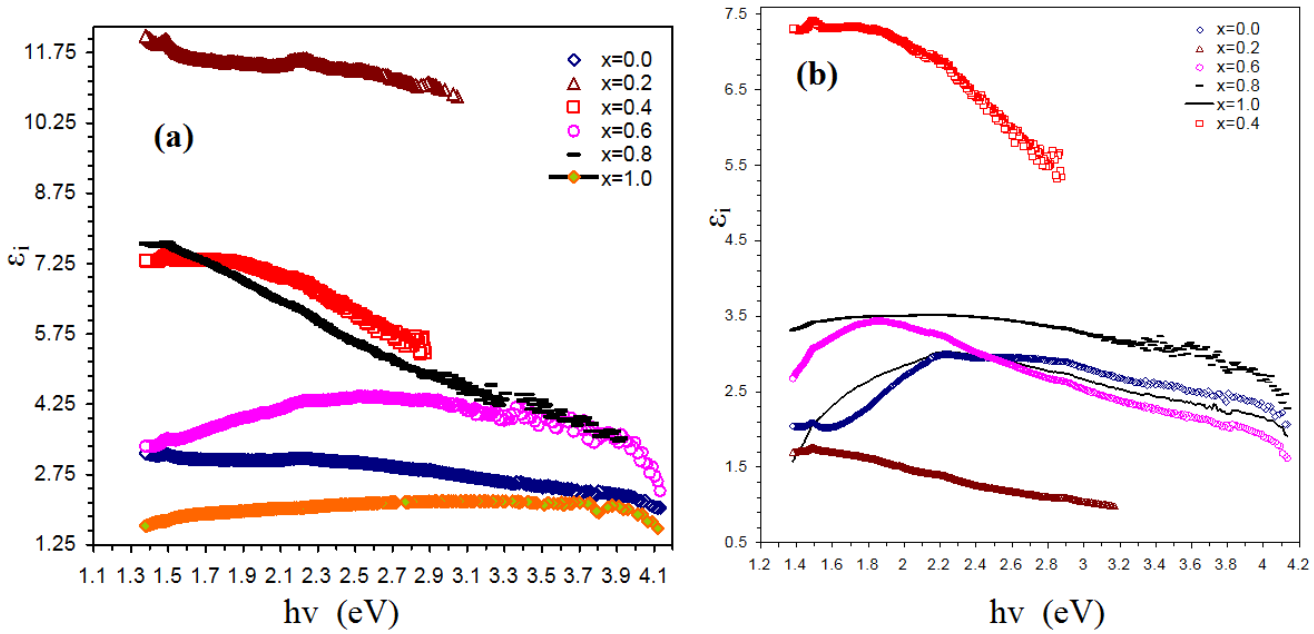


Figure (9) Shows the imaginary dielectric constant versus photon energy of thin films $Bi_2S_{3x}Se_{3(1-x)}$ compound at a-300 $^{o}$K and b-533 $^{o}$K.

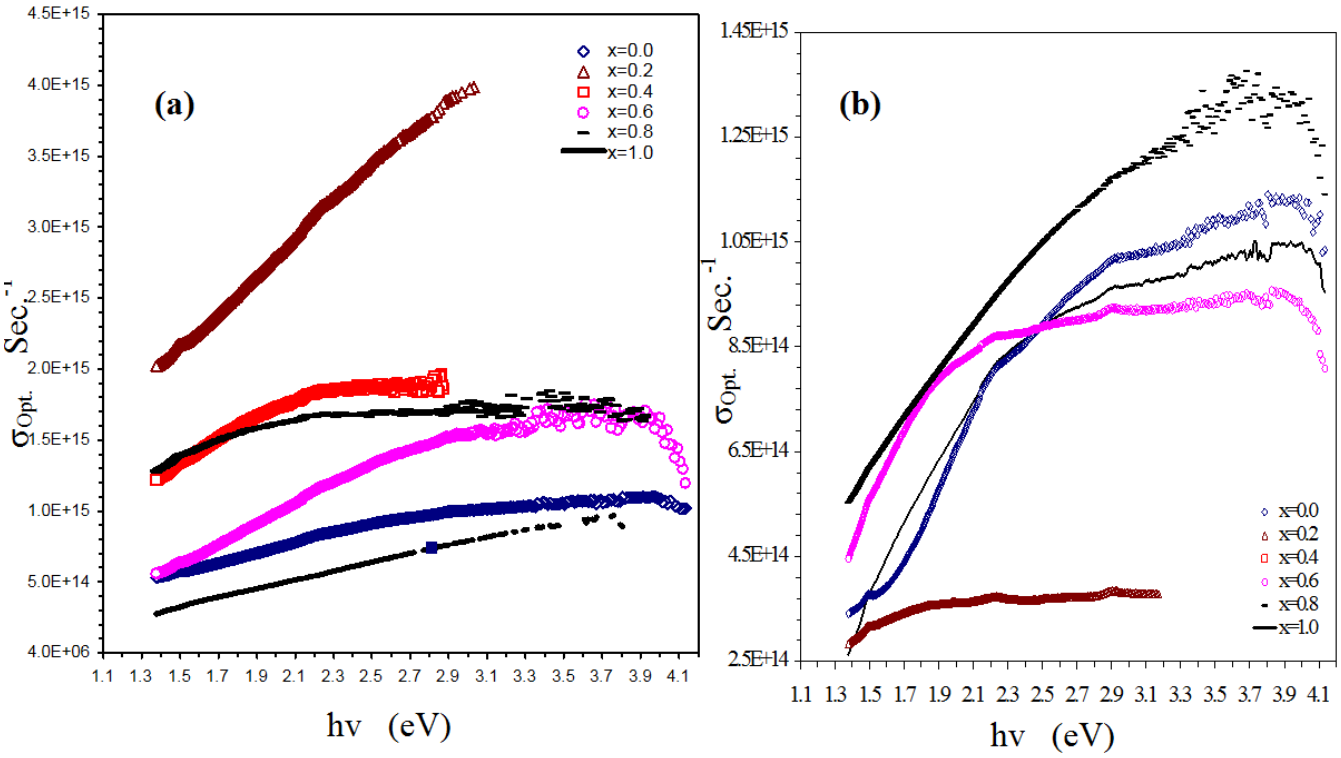


Figure (10) Shows the optical conductivity versus photon energy of thin films $Bi_2S_{3x}Se_{3(1-x)}$ compound at a-300 $^{o}$K and b-533 $^{o}$K.

**الخلاصة**

حضرت أغشية رقيقة من مركبات شبه موصلة ثنائية البزموثينايت $Bi_2S_3$ و الكواناجواتايت $Bi_2Se_3$ و مزيجهما $Bi_2S_{3x}Se_{3(1-x)}$ بطريقة التبخير الحراري في الفراغ تحت ضغط تفريغ $10^{-5}$torr على قواعد زجاجية نظيفة عند 300K و بسمك مختلف. تم دراسة التركيب البلوري للأغشية المحضرة للمركبين ومزيجهما باستخدام حيود الأشعة السينية و كانت ذات طبيعة عشوائية 300K، و تتبلور بعد عملية التلدين بتركيب متعدد البلورات عند درجة حرارة 533K، حيث أخذت تركيب معيني الأوجه للنسب (x=0.0,0.2,0.4,0.6) ومعيني قائم للنسب (x=0.8,1.0). درست الخو اص البصرية لأغشية المركبين و المزيج و التي تضمنت حساب معامل الامتصاص في مدى الأطوال الموجية (300-900)nm و حسبت فجوة الطاقة قبل وبعد عملية التلدين و التي كانت (1.75-1.84)eV و (1.74-1.7)eV للمركبين $Bi_2S_3$ و$Bi_2Se$ على التوالي. أما مزيجهما فيمتلك قيم فجوة طاقة مباشرة محصورة بين قيم هذين المركبين.