

## Laser irradiation induced phase transformation of $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$ & $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$

M.M.El-Zaida\*, Z.H.El-Gohary, M.S. AboGhazala and E.Rabiea

Physics Departement, Faculty of Science, Menoufia University, shebeen El-Koom  
Egypt

---

### ABSTRACT

*The amorphous- crystalline transition for chalcogenide semiconductor thin film inducted by laser radiation is an important topics. Study of the phase transformation and its kinetic for the two thin film  $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$  and  $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$  were followed using the change of the optical and electrical properties.*

*Transmittance (T) and Reflectance (R) were recorded in the wavelength range 200 nm-2500nm for the as prepared samples. The values of T&R were recorded again using step-wise method under the effect of accumulated laser radiation (532nm) many times. The same experiment was carried out using the change of the electrical resistance(r) of these two samples at the three isothermes 30,50 and 100°C.*

*The change of optical properties T&R and the change of the electrical resistance were employed to study the amorphous-crystalline transformation under the effect of accumulated laser radiation. The obtain results show that the energy of phase transformation were 10.22 K.cal  $\text{K}^{-1}\text{mol}^{-1}$  and 17.36 K.cal  $\text{K}^{-1}\text{mol}^{-1}$  for  $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$  &  $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$  respectively. The formed crystalline phases were identified by using X-ray diffraction patterns and SEM micrographs.*

---

### INTRODUCTION

Chalgoneide based thin films can be used as wide band gap high power device, surface devices and as high sensitive interface detectors. They behave as semiconductors and exhibit amorphous semiconductor behavior with band gap energy ranging from 1ev to 3ev (1-3). Both amorphous and crystalline forms are suitable for application due to special properties on interaction with light (4-6). Thin film chalcogenide glasses are known to be sensitive to absorption of electromagnetic radiation and show variety of photon-induced effects as result of illumination(7-8). On exposure to light capable of exciting electron-hole pairs, chalgconeide glassy materials can exhibit structure changes(9).The phase- change processes in chalgconeide were carried out by photo crystallization by Ar ion laser(10).

The purpose of present work is to report the disorder-order phase transformation of the samples  $\text{Se}_{82.05}\text{S}_{5.51}\text{Te}_{12.8}$  and  $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$ .

Also the kinetic of the crystallization processes will studied to obtain the rate of crystallization and the energy required for amorphous-crystalline transition. This will confirmed by using X-ray diffraction and SEM imaging at different laser exposure time .

### MATERIALS AND METHOD

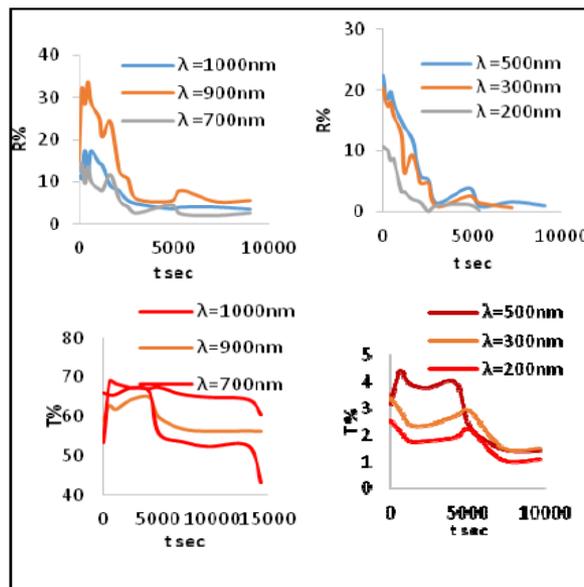
Glassy alloys of the samples  $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$  and  $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$  were prepared by using melt quenching technique. The proper ratio of the pure elements (purity 5N) were adjusted and melted in silica tube under the vacuum ( $10^{-4}$  torr) . The melted materials were kept 15h at 700 °C to insure good melting and best homogeneity. The melted samples were quenched in ice-water. The X-ray diffraction confirms the amorphous nature of the ingot samples. The thin films of these two samples were prepared using femto pulsed laser deposition techniques on quartz substrate. The obtain thickness was determined using ZYG-Omaxim-G-P and found to be in range 55-65  $\mu\text{m}$ . The optical transmittance and optical reflectance of these thin films were recorded in the wavelength range 250-2500nm using JAcO-V500 UV/Vis/NiR computerized spectrophotometer.

The irradiation laser wavelength source was green 532nm, power 100mW and fixed at 40 cm from the irradiated thin films.

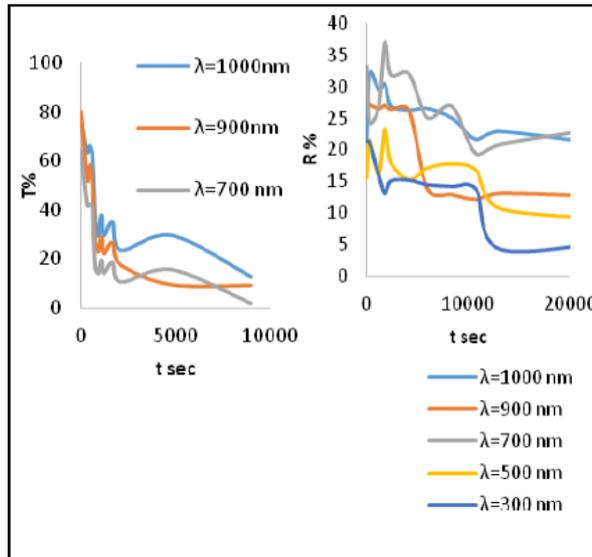
The electrical resistance of this thin films were determined using two prob-method.

### RESULTS AND DISCUSSION

The transmittance (T) and reflectance (R) of the  $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$  and  $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$  thin film samples were recorded in the wavelength range 250-2500nm for the as prepared samples . The values of T and R were recorded again under the effect of laser beam irradiation ( $\lambda=532\text{nm}$ .power=100mW at distance 40 cm) for successive different exposure times using step-wise method. This process was repeated many cycles till the values of T and R look like to be constant with respect to the location and intensities of their peaks. The values of T and R at selected wavelengths covering ,ultraviolet ,visible and infrared regions were determine from each cycle , and redrawn against the laser exposure time as in figures (1,2)



**Fig(1)** T and R against exposure time for  $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$

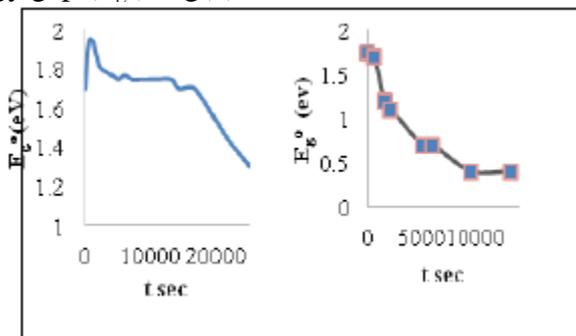


**Fig(2)** T and R against exposure time for  $Se_{87.41}S_{4.03}In_{8.56}$

From figures (1,2) the start values of each T and R are the highest. As the laser exposure time increase the values of T and R decreases. The decrement of T and R was sharp at the first and then become slow till reaching minimum constant values. The whole exposure time during T&R decrease is time of disorder- order phase transformation. This time can be divided into nucleation time through which the embryos of the growth were born and search around to the best conditions to grow and reach the critical size. If this critical size was reached it will continue to grow. Otherwise it will disappear due to the fluctuation of meta- stable phase of very short half life time. This may be the cause of why the nucleation period is mostly characterized by fluctuation between increasing and decreasing T and R intensities. As the embryos critical size exceeded, the threshold values, the formation of ordered stable phase start and continue. This was revealed as the intensities of T and R decrease montically to reach minimum constant values. This is the growth and crystallization time period.

During this time, the crystallization start and completed. Both of nucleation and crystallization periods are the whole time required to disorder – ordered phase transformation of each of the two samples  $Se_{82.05}S_{5.15}Te_{12.8}$  and  $Se_{87.68}S_{4.03}In_{8.56}$ .

Also the same study of the phase transformation of these two samples was carried out using the change of the optical energy gap ( $E_g^o$ ), fig(3)



**Fig(3)**change of optical energygap against exposure timeof laser irradiation.

The changes of the physical properties would be complex, but could be used to study kinetic of phase transition (13,14). The development of lasers has made it possible to introduce phase changes via light irradiation and to control the phase transition by absorption of optical photon i.e. photo-induced phase transformation (15-18). Such changes in T & R and  $E_g^o$  against laser exposure time can be taken as a measure of the rate of crystallization (K) and consequently may be analysed on the bases of Avrami's equation (19,20). This relation relating the extent crystalline (a) to the time by the equation,

$$a = 1 - \exp(kt)^n \tag{1}$$

$$\Theta = (1-a) = \exp(kt)^n$$

Where n is an exponent depending on the mechanism of crystallization process, and K is the crystallization growth rate constant containing nucleation and crystallization process.

During the transition amorphous-crystalline phase's  $\theta$  can be calculated experimentally at any time (t) by the relation

$$\theta = \frac{H_c - H_t}{H_c - H_a}$$

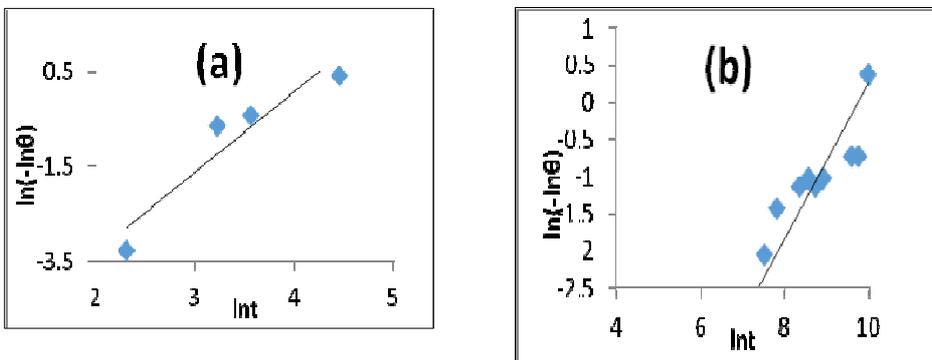
Where  $H_c$ =stands for  $T_c$ ,  $R_c$  and  $(E_g^o)_c$

$H_a$ =stands for  $T_a$ ,  $R_a$  and  $(E_g^o)_a$

$H_t$ = stands for  $T_t$ ,  $R_t$  and  $(E_g^o)_t$

The values of n of Avrami's equation can be obtained by drawing  $\ln(-\ln\theta)$  against  $\ln(t)$  according to the relation,fig(4)

$$\ln(-\ln\theta) = n \ln k + n \ln t \tag{2}$$



**Fig(4)** relation between  $\ln(-\ln\theta)$  and  $\ln t$  for (a)  $Se_{82.05}S_{5.15}Te_{12.8}$  (b)  $Se_{87.41}S_{4.03}In_{8.56}$

The values of n calculated from the slope of these curves as well as the values of K were obtained and tabulated in tables (1,2,3,4).

**Table(1)**

$Se_{87.41}S_{4.03}In_{8.56}$						
	N					
$\lambda$ (nm)	$\lambda=1000$	$\lambda=900$	$\lambda=700$	$\lambda=500$	$\lambda=300$	$\lambda=200$
R	1.1788	1.0826	1.0777	1.299	2.059	-
T	1.33	2.369	2.0101	1.5509	1.5753	2.2766
$E_g$	1.0538					

**Table(2)**

Se <sub>82.05</sub> S <sub>5.15</sub> Te <sub>12.8</sub>						
	N					
λ(nm)	λ=1000	λ=900	λ=700	λ=500	λ=300	λ=200
R	1.2551	1.2081	1.0699	1.1791	1.3282	2.4473
T	1.0275	1.0903	1.109			
Eg	1.7022					

The fractional values of n were reported by many Author (13,14).the value of n=1 is corresponding to one dimensional growth (21,23). The value of n=2 is corresponding to one dimensional growth in addition to nucleation process.

**Table(3)**

Se <sub>82.05</sub> S <sub>5.15</sub> Te <sub>12.8</sub>			
R	K	T	K
λ(nm)		Wavelength	
1000	5.95E-05	1000 nm	0.000283
900	5.66239E-05	900nm	0.000548
700	0.000224	700 nm	0.000579
500	8.79523E-05		
300	5.1957E-05		
200	8.44302E-09		

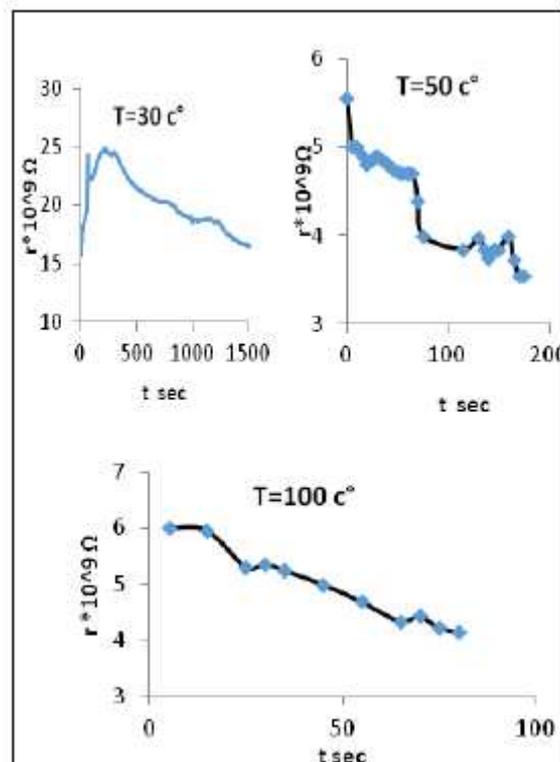
**Table(4)**

Se <sub>84.68</sub> S <sub>4.03</sub> In <sub>8.56</sub>			
R	K	T	K
λ(nm)		λ(nm)	
1000	0.000675	1000 nm	1.22933E-05
900	3.42364E-05	900nm	1.04951E-07
700	0.000188	700 nm	3.83768E-07
500	8.79523E-05	500 nm	2.1056E-06
300	3.80143E-06	300 nm	4.90328E-06
200	2.32219E-08	200 nm	3.75141E-08

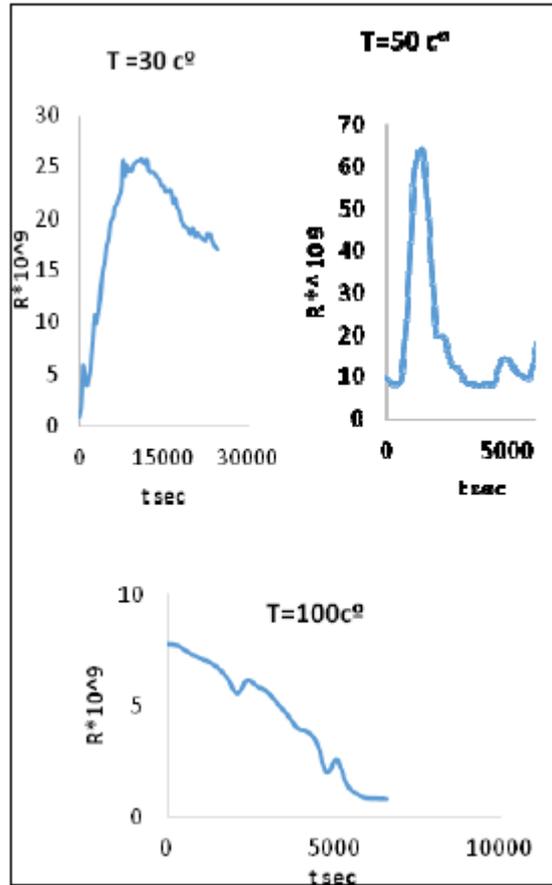
These tables show that the value of  $K$  is almost constant for every sample. This means that, the change of  $T$ ,  $R$  and  $E_g^0$  against the laser exposure time can be taken as a measure for crystallization process of the two samples  $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$  &  $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$ .

### Laser irradiation effect on the electrical resistance:-

The change of the samples electrical resistance( $r$ ) was carried out at  $30\text{ }^\circ\text{C}$ ,  $50\text{ }^\circ\text{C}$  and  $100\text{ }^\circ\text{C}$  isothermal temperature separately. The three isothermal temperatures  $30\text{ }^\circ\text{C}$ ,  $50\text{ }^\circ\text{C}$  and  $100\text{ }^\circ\text{C}$  were selected to be below the glass transition temperature ( $T_g$ ) (22) of each of the two samples  $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$  &  $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$  on the light of DTA. This selection was done to ensure that any phase transformation is only due the effect of the laser irradiation and there is no any thermal effect. The electrical resistance was recorded as function of laser exposure time at fixed temperature. The obtained results were illustrated in fig [5,6] for  $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$  &  $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$  at, isothermal  $30\text{ }^\circ\text{C}$ ,  $50\text{ }^\circ\text{C}$  and  $100\text{ }^\circ\text{C}$ .



**Fig (5)** the change of electrical resistance against laser exposure time for  $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$



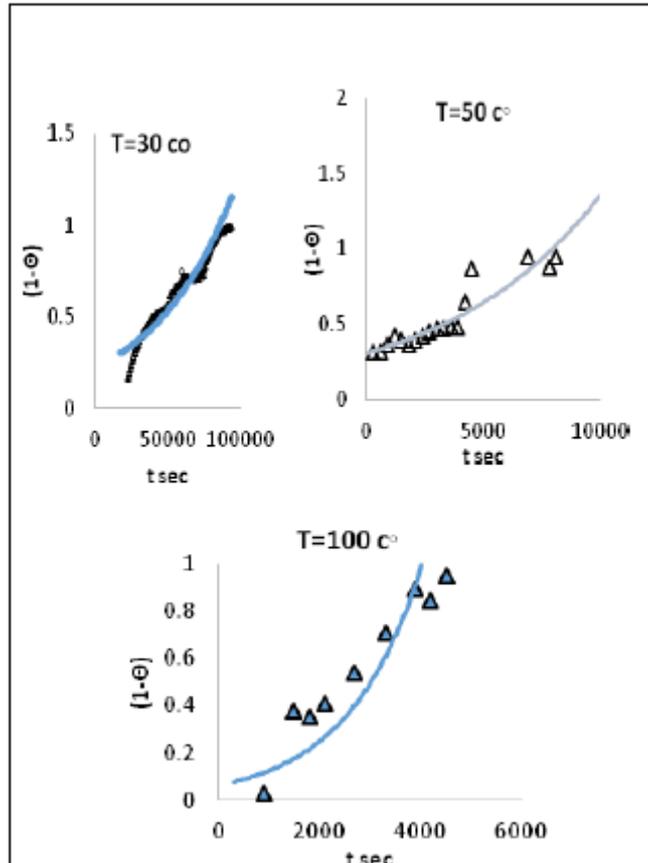
**Fig (6)** the change of electrical resistance against laser exposure time for  $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$ .

These two figures illustrate that, the electrical resistance( $r$ ) changes as function of laser exposure time in the following manner. The electrical resistance starts to increase as the exposure time increase reaching to maximum value and start to decrease montically to reach minimum saturated value as the laser exposure time increases. This behavior was noticed at  $30\text{c}^\circ$  only for sample  $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$  which means the whole time of transformation is two parts. The first is induction period through which the resistance increases to reach maximum to complete the nucleation process. After that the resistance decreases montically to reach constant value during which the crystallization process start and gradually the crystalline phase grow to reach maximum value at minimum saturation point. This behavior was detected for the sample  $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$ at each of the two isotherms  $30\text{c}^\circ, 50\text{c}^\circ$  .

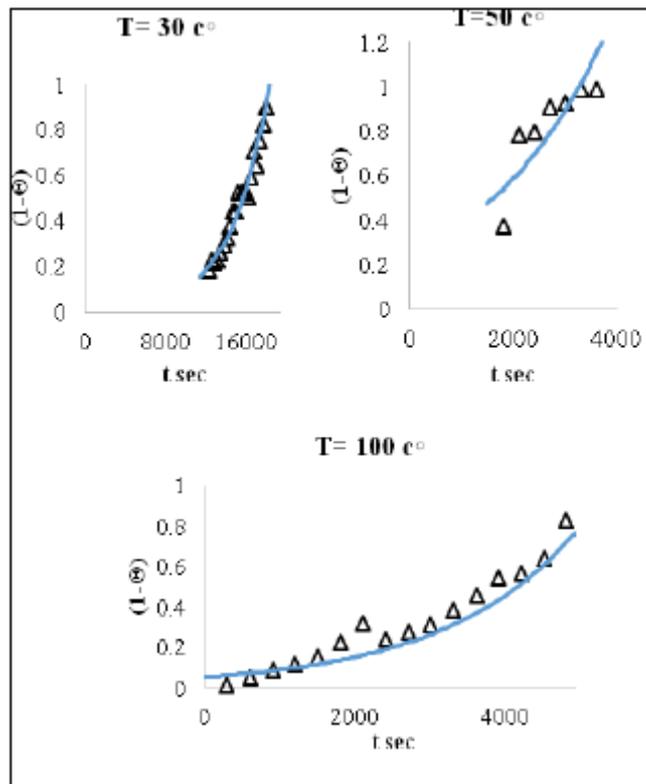
At the two isotherms  $50\text{c}^\circ$  and  $100\text{c}^\circ$  for the sample  $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$  and at only  $100\text{c}^\circ$  for the sample  $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$ , the crystalline phase start to grow from beginning. This was revealed as the electrical resistance decrease montically as the laser exposure time increase. This indicates that the nucleation period under this condition was very short and can't detect.

#### **Isothermal kinetic of phase transformation:-**

The change of the electrical resistance( $r$ ) during the crystal growth period can be used to follow the crystallization process using Avrami model . The relation between ( $\theta$ ) and  $t$  shows a homogeneous crystallization as in fig(7)



**Fig (7)** relation between  $\theta$  with time for sample  $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$



**Fig (8)** relation between  $\theta$  with time for sample  $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$ .

The value of the exponent (n) of avrami's equation can be obtained from the relation(2).The obtained values of k for each sample at each isotherm were constant and given in table (5)

**Table(5)**

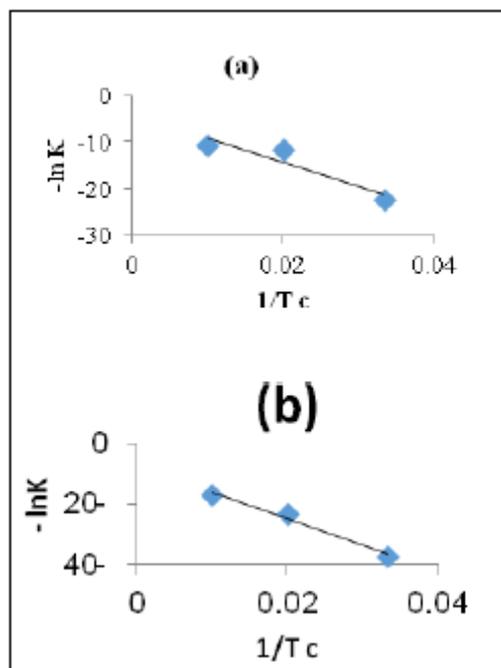
Sample	Temp c°	n	k
<b>Se<sub>82.05</sub>S<sub>5.15</sub>Te<sub>12.8</sub></b>	30	2	1.99867E-10
	50	1.5007	1.05E-05
	100	1.3477	2.1956E-05
<b>Se<sub>84.68</sub>S<sub>4.03</sub>In<sub>8.56</sub></b>	30	2	2.96034E-09
	50	1.6	1.85287E-05
	100	1.3	2.15992E-05

The energy of crystallization using laser irradiation at 30 c°, 50 c° and 100 c° can be calculated from the dependence of the crystallization rate (k) on the temperature using the equation(3)

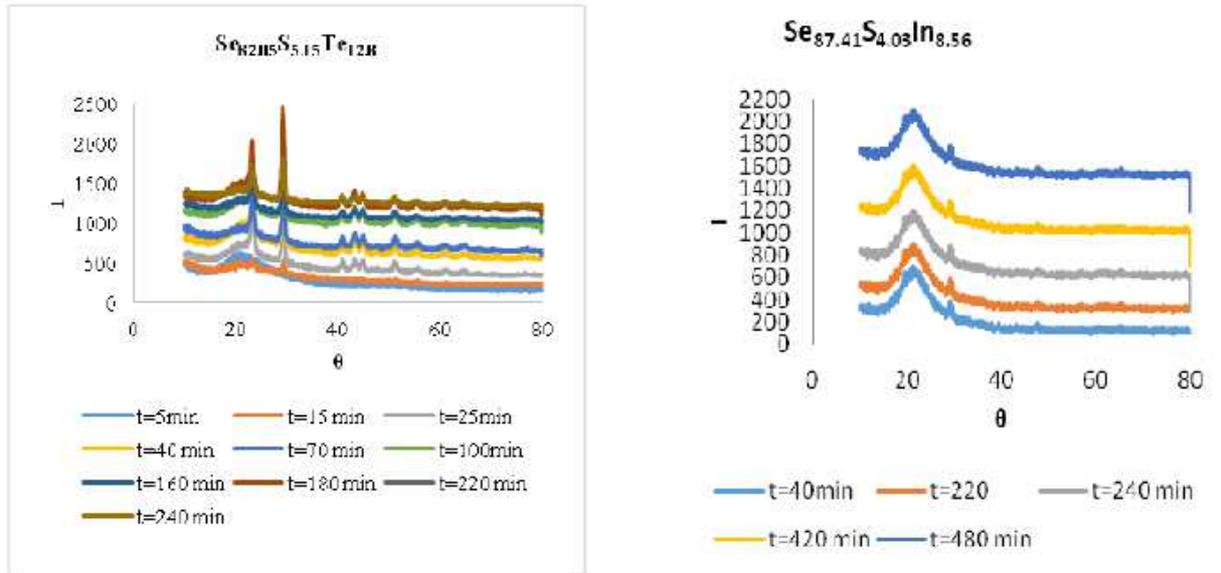
$$K = k_0 \exp(-E_c/RT) \quad (3)$$

Where K<sub>0</sub> is a constant, R is the universal gas constant, E is the energy of crystallization and T is the absolute temperature.

The variation of -lnK with 1/T is shown in fig [9] for Se<sub>82.05</sub>S<sub>5.15</sub>Te<sub>12.8</sub> and Se<sub>87.41</sub>S<sub>4.03</sub>In<sub>8.56</sub>.



**Fig (9)** Relation between K and 1/T samples(a)Se<sub>82.05</sub>S<sub>5.15</sub>Te<sub>12.8</sub>&(b)Se<sub>87.41</sub>S<sub>4.03</sub>In<sub>8.56</sub>.



**Fig(10)** x-ray diffraction of two thin film samples  $Se_{82.05}S_{5.15}Te_{12.8}$  &  $Se_{87.41}S_{4.03}In_{8.56}$ .

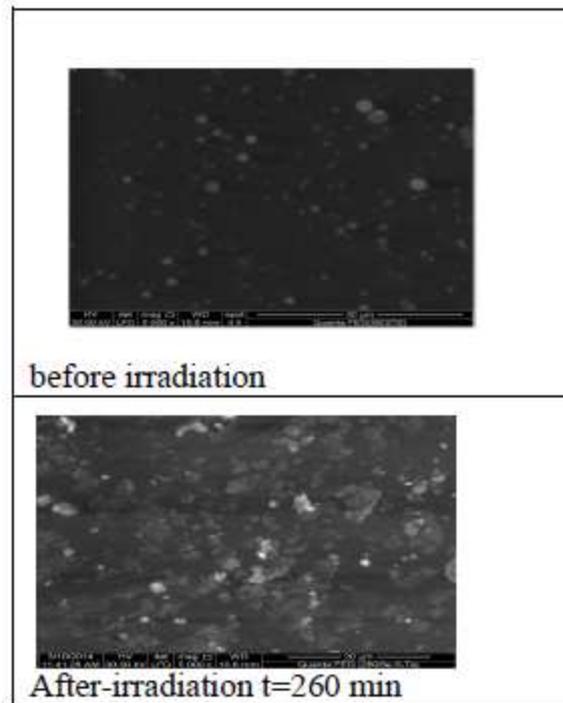
This relation mostly straight line. This means that the disorder order phase transformation process is only due to laser irradiation without any thermal effect. The values energy of crystallization for the two sample  $Se_{82.05}S_{5.15}Te_{12.8}$  and  $Se_{84.68}S_{4.03}In_{8.56}$  were given in table(6).

**Table(6)**

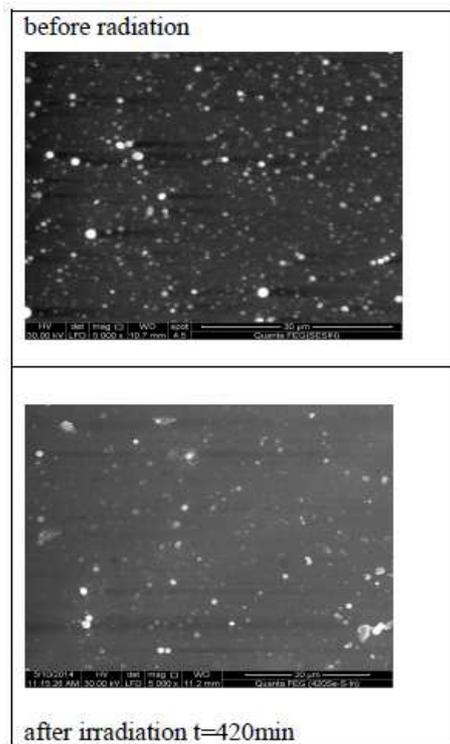
Sample	$Se_{82.05}S_{5.15}Te_{12.8}$	$Se_{87.41}S_{4.03}In_{8.56}$
Ec	10.22655	17.35564445
Kcal		
$K^{-1}mol^{-1}$		

The x-ray diffraction was used to follow the phase transformation as well as the SEM micrographs in step-wise as the laser exposure time increase.

Figure (10-12) show that, the formed crystalline phases were  $Se_{7.68}Te_{0.32}$ ,  $SeS$ ,  $S_2Te$ ,  $Se_2S_2$  for the sample  $Se_{82.05}S_{5.15}Te_{12.8}$  and  $SeS_{10}$ ,  $Se_3In_2$ ,  $Se_{2.4}S_{0.6}In_2$ ,  $SIn$  for sample  $Se_{87.41}S_{4.03}In_{8.56}$ . The SEM micrograph confirms the unidimensional growth of the crystalline phases.



**Fig (11)** SEM of of two thin film sample  $\text{Se}_{82.05}\text{S}_{5.15}\text{Te}_{12.8}$



**Fig (12)** SEM of of two thin film samples  $\text{Se}_{87.41}\text{S}_{4.03}\text{In}_{8.56}$ .

## CONCLUSION

The changes of transmittance (T), reflectance (R), optical energy gap ( $E_g^o$ ) and the electrical resistance (r) with laser exposure time were used as indication about the transformation of the two samples  $Se_{82.05}S_{5.15}Te_{12.8}$  &  $Se_{87.41}S_{4.03}In_{8.56}$  from disordered to ordered state. Avrami's crystallization method was applied to the change of T, R,  $E_g^o$  and r against the laser exposure time and to get Avrami's exponent (n), crystallization rate (K) and the energy of crystallization  $E_c$  have been calculated. The laser beam is found to be a powerful tool for the photo induced phase transformation of the two samples  $Se_{82.05}S_{5.15}Te_{12.8}$  &  $Se_{87.68}S_{4.03}In_{8.56}$ . x-ray diffraction and SEM confirm, the process of phase transformation and identify the formed crystalline phases for each samples as well as the shape of the crystal growth.

## REFERENCES

- [1]. J.C.Osvwa, C.I Oriku, J. Of Non-oxide glasses Iss1, (2010)
- [2]. J.C.Osvwa, C.I Oriku, C.M. Atuloma, chalcogenide letter, 6, Iss. 6, (2010)
- [3]. J.C.Osvwa, C.I Oriku, OI. Vko, chalcogenide letter, 7, no. 7, (2010)
- [4]. A. Iorinczi, E. sava, A. Angel, J. opt. Adv. Mater. 6(1), 349 (2004)
- [5]. C.I. Oriaku, J.C. Osvwa, C.H. Njokv, Journal of Non-oxide Glass vol. 3, No. 1, 2011, p25-30.
- [6]. C.I. Oriaku, J.C. Osvwa, Journal of ovonic Research. 5, no6, (2009).
- [7]. S. Ilican, Y. Caglar and M. calgar, physica Macedonica, 56, 43 (2006)
- [8]. I.C. Osvwa, C.I. Oriaku, Journal of Non-oxide Glass vol. 2, No. 1, 2010, P. 1-5.
- [9]. Adam A., Bahisti, M.A. Majeed khan, S. Kumar, M. Husain and M. Zulfequar, chalcogenide Letters 4, 155 (2007)
- [10]. M.I. Abd-Elrahman, Rasha. M., Shiamaa A, Hafiz M, Thermo chimica Acta vol. 575, (2014) P285-290.
- [11]. D. Stand, J. optoelectronics and Adv. Materials 7, 1679 (2005)
- [12]. M.K. El-Mously & M.M. El-Zaidia, J. non-Cryst solids Vol. 11 No. 5 March (1973) P. 519
- [13]. N. Jain, Indian. J of technology 8, 356 1970
- [14]. K. Nasu Relaxation of excited state and photo-induced structural phase transformation (springer – verlag, Berlin 1997)
- [15]. Wilson Quevedo, Marcel Petri, Gerhard Busse and Simone Techert the Journal of chemical physics 129, 024502 (2008)
- [16]. Balbirsingh patial, Nagesh Thakur & S.K. Tripathi J. of Nano and electronic physics Vol. 5 No. 2, 02017 (4 PP) (2013)
- [17]. V.K. Malinovsky, N.V. Surovtse V., of chalcogenide letters Vol. 9, No. 2 Feb 2012, P 79 – 84.
- [18]. M. Avrami, J. chem phys. 7, 1103 (1939), 8 – 212 (1940), 9 – 177 (1941)
- [19]. K.P. Momedov and Z. Narieva SOV phy. Cryst, 9 – 211 1964
- [20]. J.N. Hay, Br. Polym. J 3, 74, 1971
- [21]. D. Turnbull, J.C. Fisher., J. chem. Phys., 17, 71, 1949