National Conference on Recent innovations in Applied Sciences and Humanities' NCASH-2015 | Volume : 4 | Issue : 10 | Special Issue Oct- 2015 • ISSN No 2277 - 8179

CRYSTALLIZATION KINETICS IN GLASSY $Se_{70}Te_{30}$-$_{X}Ag_{X}$ (x = 0, 2, 4, 6) USING ISO-CONVERSIONAL TECHNIQUE

Physics

KEYWORDS: Chalcogenide glasses, Activation energy, Crystallization kinetics, DSC, Iso-conversional methods

R. Shukla	Department of Physics, D.B.S. College, Kanpur, India,
P. Agarwal	Department of Physics, D.B.S. College, Kanpur, India,
Suresh K. Sharma	Department of Physics, Harcourt Butler Technological Institute, Kanpur, India
A. Kumar	Department of Physics, Harcourt Butler Technological Institute, Kanpur, India

ABSTRACT

In the present paper calorimetric analysis of glassy $Se_{70}Te_{30}$-$_xAg_x$ (x = 0, 2, 4, 6) has been carried out using Differential Scanning Calorimetry at various heating rates (5 - 20 K/min). Crystallization temperature increases on increasing the heating rate. Activation energy of crystallization (E_c) is calculated using five different iso-conversional methods. It is observed that Ec depends on the extent of crystallization. At a particular extent of crystallization, Ec shows a reversal in the trend at 4 at. % of Ag, which is explained in terms of mechanically stabilized structure at this composition.

INTRODUCTION

Field of chalcogenide glasses has always been an area of great interest because of their promising technological applications in optical fibres, photo resistors, photoconductors and reversible phase change optical recording. Our need for storage is increasing with an exponential rate. Therefore, erasable recording is considered to be a potential replacement for conventional recording due to its high storage density and stability [1-11]. For this reason Se has become a material of great commercial interest.[7-12].

Se-Te alloys are extensively used in optical phase change applications [13-14]. In spite of being more advantageous there are certain limitations of these alloys like limited reversibility [15]. To overcome certain problems, third additive is also added to this binary system.

In the present paper Ag is added to binary $Se_{70}Te_{30}$ system and activation energy of crystallization is calculated. Ag doped chalcogenide glasses, is studied by some workers [16-30] considering activation energy of crystallization to be constant during the process of crystallization. Crystallization kinetics of ternary $Se_{70}Te_{30}$-xAgx (x = 0, 2, 4, 6) glasses is studied using iso-conversional methods and dependence of activation energy of crystallization (E_c) on extent of crystallization is studied. E_c plays a vital role in deciding these materials for optical phase change recording devices [31-32]. To calculate E_c, five different iso-conversional methods are used i.e., Kissinger – Akahira - Sunose [KAS] [33-35], Friedman [36], Flynn - wall - Ozawa [FWO] [37], Friedman – Ozawa [FO] [38] and Starink [39] methods.

THEORETICAL BASIS

Differential scanning calorimetry (DSC) is valuable technique for the quantitative study of crystallization in different glassy systems and has been widely used [40-45]. Most of these treatments are based on the following relation:

$$\alpha = 1- \exp[-(K\,t)^n] \qquad (1)$$

where α is extent of crystallization and K is rate constant which is thermally activated [46-48].

In all non-isothermal methods one assumes a constant heating rate that is $T = T_o + \beta.t$, where To is the initial temperature. The best description of these methods is an iso- conversion method.

Kissinger-Akahira-Sunose (KAS) Method

In the KAS method, the relation between the temperature $T_{\alpha i}$ and the heating rate β is given by

$$\ln = c\left(\frac{\beta}{T_{\alpha i}}\right)\text{onstant} - \frac{E_{c\alpha}}{RT_{\alpha i}} \qquad (2)$$

Plots of $\ln\left(\frac{\beta}{T_{\alpha i}}\right)$ vs. $1000/T_{\alpha i}$ are plotted and activation energy $E_{c\alpha}$ is calculated from the slopes of these plots.

Friedman Method

For various heating rates β, the Friedman method can be used at a specific crystallization fraction α as

$$\ln\left(\frac{d\alpha}{dt}\right) = constant - \frac{E_{c\alpha}}{RT_{\alpha i}} \qquad (3)$$

The parameter Ecα at a specific value of α, is then calculated from a plot of ln (dα/dT) αi vs. 1000 / T αi across different heating rates. The process is repeated for different values of α.

Flynn-Wall-Ozawa Method (Fwo)

The Flynn-Wall-Ozawa (FWO) method has been developed for non-isothermal analysis of crystallization in which final reaction is as follows

$$\ln(\beta) = \text{constant} - 1.0518\left(\frac{E_{c\alpha}}{RT_{\alpha i}}\right) \qquad (4)$$

By plotting ln β vs. $1000/T_\alpha$ for the chosen value of α, activation energy E_c is determined.

Friedman-Ozawa Method (FO)

According to Friedman-Ozawa method a linear relationship of ln (β.dα / dT) vs. 1000/T exists with slope proportional to E_c which can be calculated from different temperature data for fixed value of fraction transformed α by the following relation:

$$\ln\left(\beta.\frac{d\alpha}{dT}\right) = \frac{-E_c}{RT} + \text{constant} \qquad (5)$$

Starink Method

The KAS and FWO methods can be expressed in general form, i.e.,

$$\ln\left(\frac{\beta}{T^s}\right) = \frac{-AE_c}{RT_f} + \text{constant} \qquad (6)$$

where Tf is the temperature at which a fixed fraction α of the total amount is transferred.

In the method proposed by Starink
A=1.0008 and s = 1.92 i.e.

$$\ln\left(\frac{\beta}{T^{1.92}}\right) = \frac{-1.0008E_c}{RT_f} + \text{constant} \qquad (7)$$

EXPERIMENTAL

Samples of glassy $Se_{70}Te_{30}$-xAgx are prepared in bulk form by conventional melt quenching technique. X-ray diffraction pattern (XRD) of the samples confirmed the glassy nature of the material DSC measurements are done at four heating rates 5, 10, 15 and 20 K/min. The extent of crystallization (α) at any temperature (T) is calculated as α = AT /A[49].

RESULTS AND DISCUSSION

DSC thermograms for glassy alloys of $Se_{70}Te_{30}$-xAgx obtained at a particular heating rate 10 K/min. are given in Fig.1. Similar thermograms were obtained at other heating rates and for other glassy alloys used in the present study.

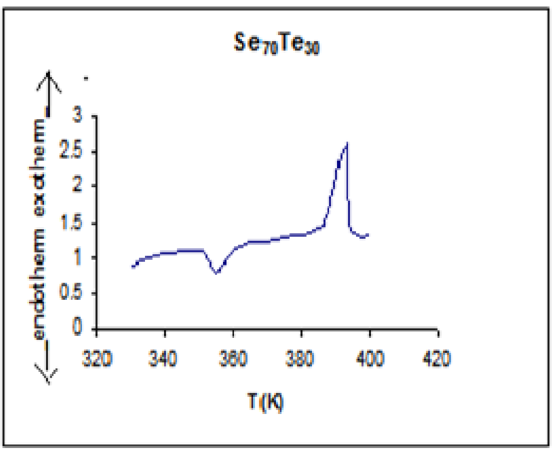

Fig.1(a): DSC Thermogram for glassy $Se_{70}Te_{30}$ at 10 K/min

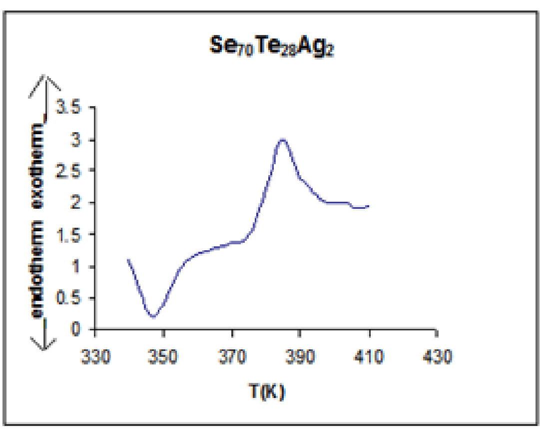

Fig.1(b): DSC Thermogram for glassy $Se_{70}Te_{28}Ag_2$ at 10 K/min

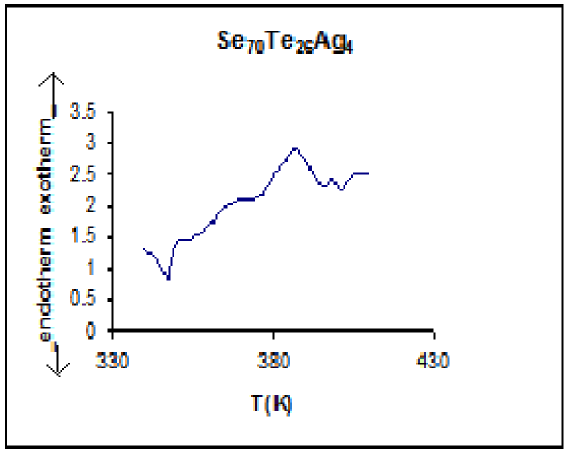

Fig.1(c): DSC Thermogram for glassy Se70Te26Ag4 at 10 K/min

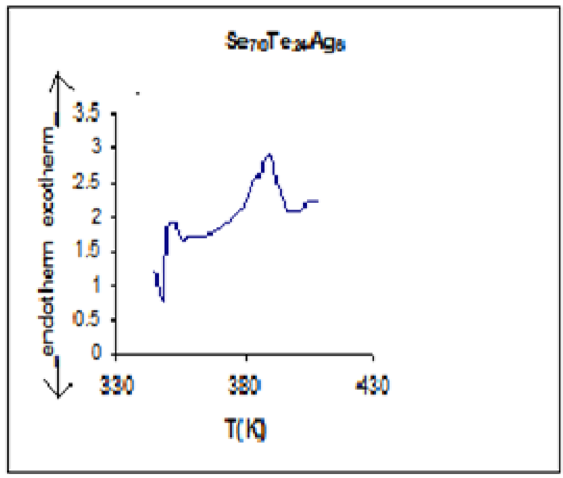

Fig.1(d): DSC Thermogram for glassy Se70Te24Ag6 at 10 K/min.

Activation Energy of Crystallization (E_c)

All of the iso-conversional methods require the determination of the temperature Ti at which a fixed fraction of the total amount is transformed. Such linear fits obtained by KAS, Friedman and Starink methods for $Se_{70}Te_{26}Ag_4$ at α = 0.5, are given in Fig. 2. Linear fits obtained by remaining two methods FWO and FO methods are given in Fig. 3 for the same composition at α = 0.5.

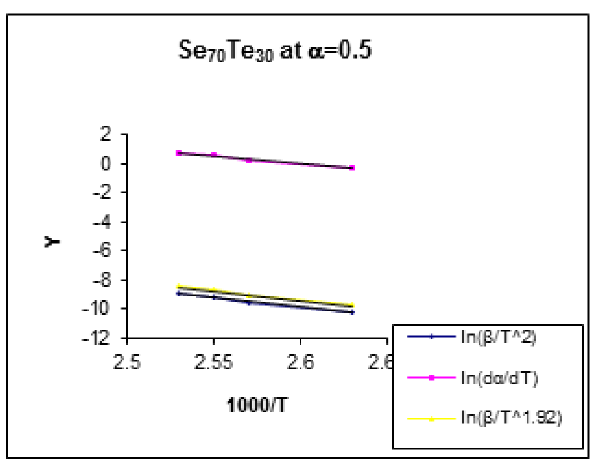

Fig.2(a)

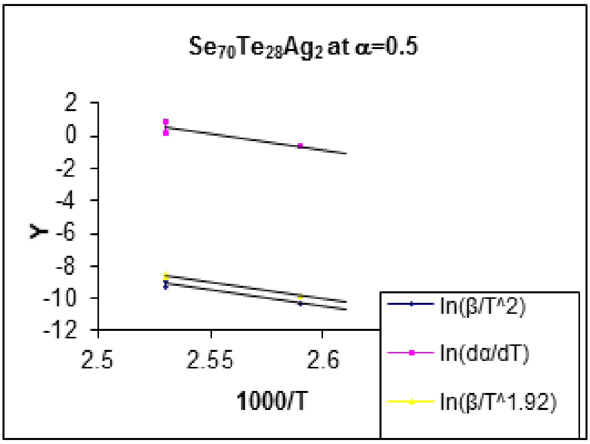

Fig.2(b)

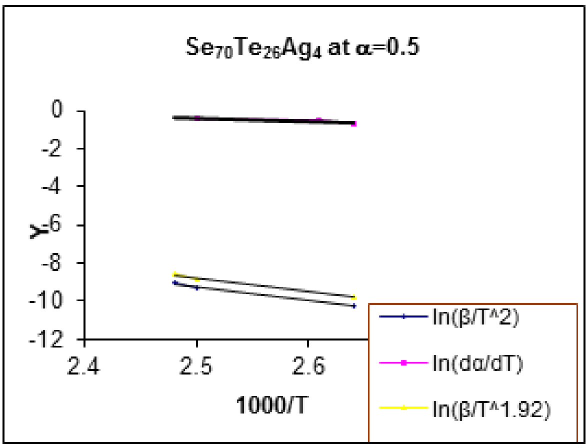

Fig.2 (c)

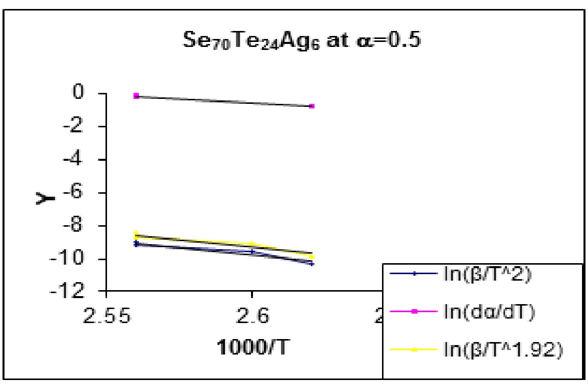

Fig.2(d)

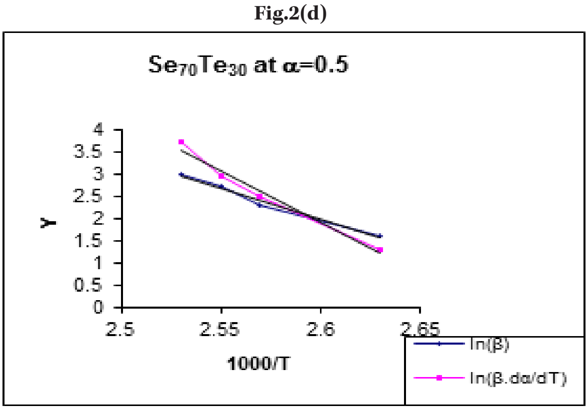

Fig.2(e)

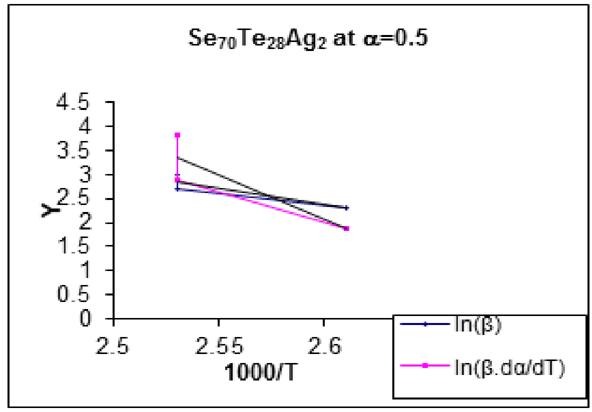

Fig.2(f)

Fig.2(a-f): Linear plots in case of KAS, Friedman & STARINK methods at α = 0.5

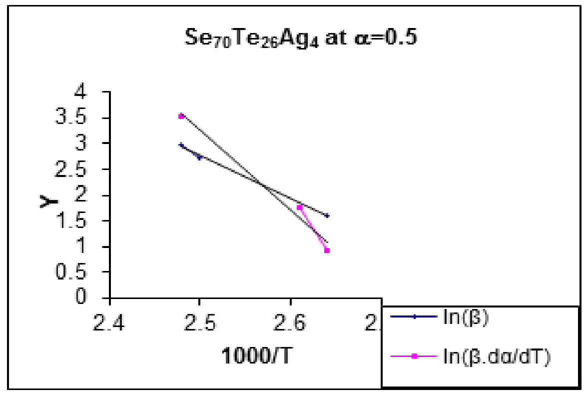

Fig.3(a)

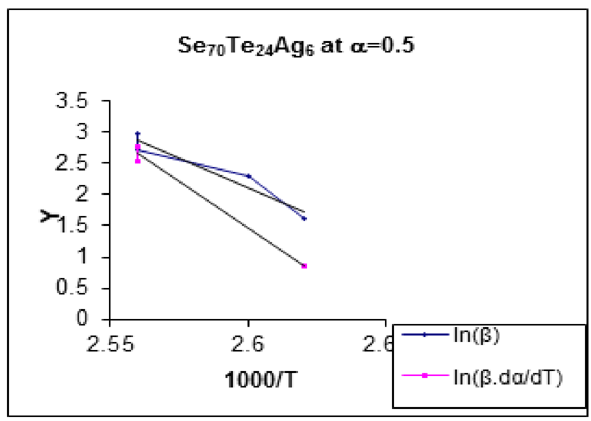

Fig.3(b)

Fig.3: Linear plots in case of FWO, FO methods at α = 0.5

Linear fits are obtained at different values of **α** and by measuring the slopes of these linear fits, E_c is calculated. The values E_c for $Se_{70}Te_{26}Ag_4$ are given in Tables 1.

TABLE - 1
ACTIVATION ENERGY EC (eV) FOR Se70Te26Ag4 AT DIFFERENT α

α	KAS	Friedman	FWO	FO	Starink
0.3	0.50	0.52	0.68	1.23	0.34
0.4	0.63	0.29	0.67	0.96	0.30
0.5	0.64	0.13	0.68	1.34	0.64
0.6	0.60	0.59	0.64	1.18	0.59
0.7	0.62	0.60	0.57	1.16	0.61

0.8	0.59	0.59	0.62	1.20	0.59
0.9	0.58	0.77	0.62	1.41	0.59

The results of Ec calculated for $Se_{70}Te_{26}Ag_4$ for various values of at α are given in Table-3.

It is clear from the above table that the values of E_c are not same at different stages of transformation. Figure 4 (a, b and c) shows variation of activation energy as a function of degree of conversion α as observed by all iso-conversional methods used in the present study for glassy $Se_{70}Te_{26}Ag_4$. Similar results were found for the glasses.

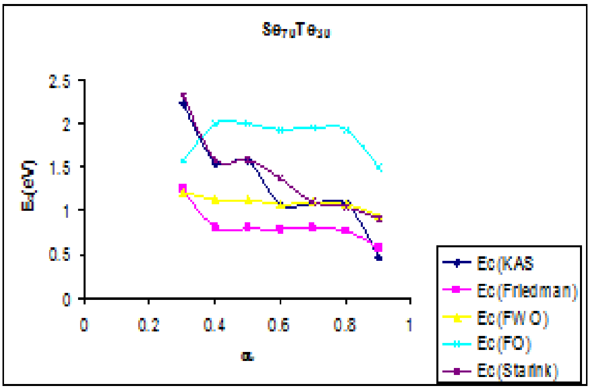

Fig.4(a)

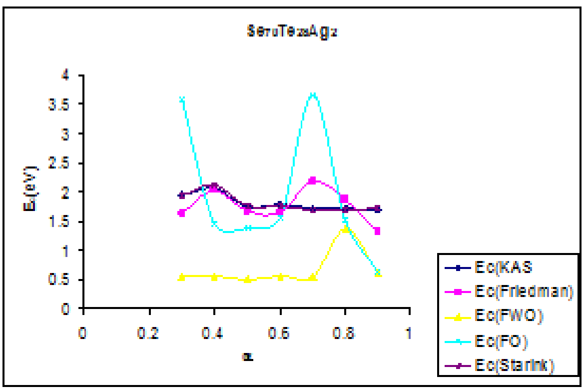

Fig.4(b)

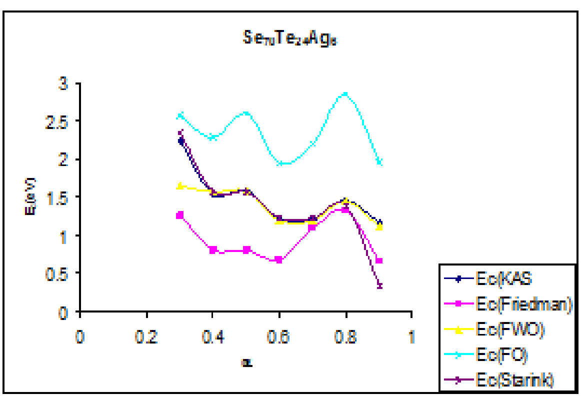

Fig.4 (c)

Fig. 4(a-c): Variation of activation energy Ec with extent of crystallization

The observed difference in the values of E_c evaluated by different methods may be attributed to the different approximations that have been adopted while arriving at the final equation used in different methods.

Activation energy is found to be dependent on the addition of third element Ag, which is shown in Fig. 5 at α = 0.5 and α = 0.7. Similar trends were obtained at other values of α

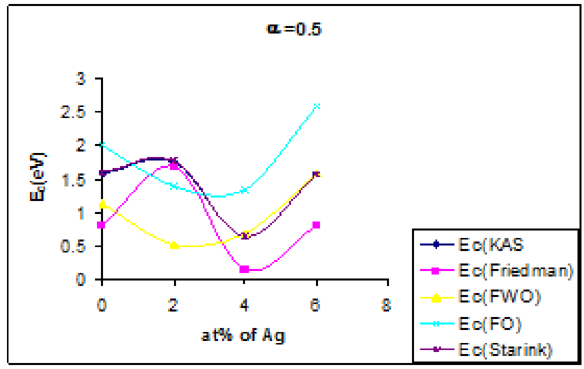

Fig 5(a): Composition dependence of activation energy of crystallization at α = 0.5.

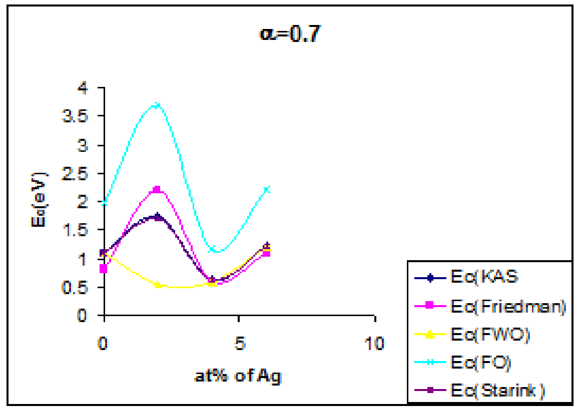

Fig 5(b): Composition dependence of activation energy of crystallization at α = 0.7

Above figures show that activation energy varies according to atomic percentage of third additive Ag . Initially, activation energy Ec increases on adding the third additive Ag. But it shows a trend reversal at 4 at% of Ag, where it shows a minima. Similar kind of discontinuity is reported in various physical parameters [59-60] in chalcogenide glasses when average co-ordination number <r> reaches 2.4. This is explained by Phillips and Thorpe in terms of mechanically optimized structure at critical glass composition [61-62]. The co-ordination number of Se and Te is 2 and that of Ag is 4. Hence, in glassy $Se_{70}Te_{30}$-xAgx (x = 0, 2, 4, 6), average co-ordination number comes out to be <r>=2.1. This value of <r> is lesser than 2.4. This may be due to an important limitation of Phillips & Thorpe model [63]. Phillips considered that the interaction between atoms is purely covalent while reaching at the balance condition. Such an assumption may be valid for glasses showing electronic conduction but not valid for glasses containing Ag, which shows ionic conduction [64].

CONCLUSION

DSC technique is used to study the crystallization kinetics of glassy ternary alloys in the glassy system $Se_{70}Te_{30-x}Ag_x$. Activation energy of crystallization is found to decrease with the increase in extent of crystallization. Activation energy of crystallization is found to be dependent on composition also. A discontinuity in activation energy of crystallization vs Ag concentration is observed at 4 at. % of Ag. This is explained in terms of average co-ordination number of the alloys.

REFERENCE

[1]Gosain D. P, Shimizu T., Ohmuru M., Suzuki M., Bando T., Okano S., (1991), J. Mat. Sci. 26, 3271.|[2]Uchino K., Takada K., Ohno T., Yoshida H., Kobayashi Y., (1993), Jpn. J. Appl. Phys. 31, 5354.|[3]Nobukuni N., Takashima M., Ohno T., Horie M., (1995), J. Appl. Phys. 78, 6980.| [4]Nakamura M., Wang Y., Matsuda O., Inoue K., Murase K., (1996), J. Non-Cryst. Sol. 198-200, 740.| [5]Men L., Jiang F., Gan F., (1997), Mater. Sci. Eng. B 47, 18.| [6]Woudenberg R. V., (1998), Jpn. J. Appl. Phys. 37, 2159.| [7]Babeva Tz, Dimitrov D., Kitova S., Konstantinov S. I., (2000), Vacuum 58, 496.|[8]Mikla V. I., Mikhalko I. P., Mikla V. V., (2001), Mater. Sci. Eng. B 83, 74.\| [9]Kolobov A. K., Tominaga J., (2002), J. Optoelectron. Adv. Mater. 4 (3), 679.| [10]Khan S. A., Zulfequar M., Husain M., (2003), Vacuum 72, 291.| [11]Lezal D., (2003), J. Optoelectron. Adv. Mater. 5(1), 23.| [12]Mehta N., Zulfequar M., Kumar A., (2004), J. Optoelectron Adv. Matter,6,441.|[13]Lucovsky G., Mooradian A., Taylor W., Wright G. B., Keezer R. C., (1967), Sol. Stat. commn.5,113.| [14]Lucovsky G., (1969), Mater. Res. Bull. 4, 505.|[15]A. Mooradian A., (1968), in: Proc. Of Se-Te conf..| [16]Schotmiller J., Tabak M., Lucovsky G., Ward A, (1970), J. Non-Cryst. Solids 4, 80. |[17]Das G. C., Bever M. B., Uhlmann D. R., (1972), J. Non-Cryst. Solids 7, 251.|[18]E1-Mously M. K., E1 Zaidia M. M., (1978), J. Non-Cryst. Solids 27, 265.|[19]Abkovitz M. A., (1979), in " The Physics of Se and Te" edited by E. Gerlach, P. Grosse (Springer, Berlin, p.178.| [20]Kotkata M. F., E1-Mously M. K., (1983), Acta Physica Hungarica 54(3), 303.| [21]Brown B. R., (1974), Appl. Optics 13, 761.| [22]Weiser K. , Gambino R. J., Reinhold J. A., (1973), Appl. Phys. Lett. 22, 48.|[23]Smith A. W., Appl. Optics 13, 795 (1974).|[24]K. Tanaka, (1993), J. Non-Cryst. Solids 164-166, 1179.| [25]Wagner T., Jilkova R., Frumar M., Vicek M., (1994), Int. J. Electron. 77, 185.| [26]Tanaka K., Itoh M., Yoshida N., Ghto M., (1995), J. Appl. Phys. 78, 3895.| [27]Kawaguchi T., Maruno S., Elliott S. R., (1996), J. Appl. Phys. 79, 9096.|[28]Ohto M., (1997), Phys. Status Solidi a 159, 461.| [29]Wagner T., Frumar M., Suskova V., (1991), J. Non-Cryst. Solids, 128, 197.| [30]Frumar M., Polak Z., Cernosek Z., Frumarova B., Wagner T., (1997), Chem. Papers 57, 310.| [31]T. Wagner, J. Optoelectron Adv. Matter. 4, 717 (2002).| [32]Ramesh K., Asokan S., Sagunni K. S., Gopal E. S. R., (2000), J. Phys. Chem. Solids 61, 95.|[33]Zhou G. F., (2001), Mater. Sci. Eng. A 73, 304.|[34]Gutwirth J., Wagner T., Kohoutek T., Vlcek Mir, Schroeter S., Kovanda V., Vlcek Mil, Frumar M., (2003), J. Optoelectron Adv. Matter. 5, 1139.| [35]Chou L. H., Chang Y. Y., Chai Y. C., Wang S. Y., (2001), J. Appl. Phys. Part 1 40, 4924.| [36]Kotkata M. F., Mohamed C. S., Radwan M. M., (1990), J. Mater. Sci 25, 482.| [37]Kitao M., Gotoh C., Yamada S. J., (1995), J. Mater. Sci. 30, 3521.| [38]Sharma D., Shukla R. K., Kumar A., (1999), Thin Solid Films 357, 214.|[39]Sharma D., Shukla R. K., Singh A., Nagpal A., Kumar A, (2000), Adv. Mater. Opt. Electron. 10, 251.|[40]Titus S. S., Asokan S., Gopal E. S. R., (1992), Solid State Communication 83,|[41]Vyazovkin S., (2000), New J. Chem. 24, 913.|[42]Kissinger H. E., (1956), J. Res. Nat. Bur Stand 57, 217.|[43]Kissinger H. E., (1957), Anal Chem 29,1702.|[44]Akahira T., Sunose T., (1971), Res. Rep. Chiba Inst. Technol, 16, 22.|[45]H. L. Friedman H. L., (1964), J. Polm. Sci. C6, 183.|[46]Ozawa T., (1965), Bull. Chem. Soc. Jpn. 38,1881.|[47]Flynn H and Wall A J. (1966), Polym. Sci. B 4, 323[48]Friedman L., (1964), J Polym. Sci. 6, 183.|[49]Ozawa T., (1986), J. Therm. Anal 31,547.| [50]Starink M., (1996), Thermochim. Acta 288, 97.[51]Soliman A. A, E-1-Den M. B. (2007) Chalcogenide Letters 4, 35.|[52]Ahmad A., Khan Samshad A., Khan K., Sinha K1, Zulfequar M., and Hussain M. (2007) Eur Phys J Appl Phys 38, 211.| [53]Abdel M– Satar, Abdel M. A. – Rahim and E1 – Karashy A. (2007) International Journal of Pure and Applied Physics 3, 59.| [54]Mehta N., Singh K., Kumar A. (2009), Physica B 404, 1835.|[55]Saxena Manish, Bhatnagar PK (2003) Bull Mater Sci 26:547.|[56]Mehta N., Kumar A., (2008), Phill Mag Lett 88, 793.| [57]Avrami M., (1939), J Phys Chem 7, 212.|[58]Avrami M., (1940), J Phys Chem 8, 212.| [59]Johnson W. A., Mehl R. F., (1939), Trans Am Inst Miner Eng 135,419.|[60]Mahadevan S., Gridhar A., Singh A. K., (1986), J. Non – Cryst, 88,11.| [61]Maan A. S., Goyal D.R., Kumar A., (2007), Chalcogenide Letters 4, 48.|[62]Feltz A., Aust H., Blayer A., (1983), J Non-Cryst Solids 55, 179.|[63]Agnihotri A. K., Kumar A., Nigam A. N. (1988), Philos Mag Lett 58, 63| [64]Asokan S., Parthasarthy G., Gopal E. S. R., (1988), Philos Mag B 57, 49.|[65]Phillips J. C., Thorpe M. F. (1985), Solid State Commun 53, 699.|[66]Ribes M., Bychkov E., Pradel A., (2001), J. Optoelectron. Adv. Mater. 3, 665.