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Study of Crystallization Kinetics of Some $Te_x(Bi_2Se_3)_{1-x}$ Glassy Alloys

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ABSTRACT

The activation energy plays a dominant role in deciding the utility of the material for the specific purpose - here storage. Chalcogenide glasses have been investigated intensively because of their promising technological applications in reversible phase change optical recording. The dependence of the crystalline temperature (T_c) and the peak temperature of crystallization (T_p) on the composition and heating rate (β) has been studied in the present work. From the heating rate dependence T_p, the activation energy for crystallization (E_c) has been evaluated. The activation energy E_c, calculated using three different approaches is found to increase with the increase in Te content. This analysis helps in finding the suitability of an alloy to be used in phase transition optical memories / switches. The results have been analyzed using Kissinger's equation and Marseglia's theory for non-isothermal crystallization of materials.

Keywords: Glasses-thermal properties; Chalcogenide Glasses, Glass-optical materials; Thermal Analysis; Activation energy.
PACS Codes: *65.60, 81.70P, 42.70C*

INTRODUCTION

Chalcogenide glasses are a recognized group of inorganic glassy materials which always contain one or more of the chalcogen elements Se, S or Te. They are generally less robust, weaker bounded materials than oxide glasses [1]. Chalcogenide glasses have been attracting much attention in the field of electronics as well as in infrared optics, since they exhibit several peculiar phenomena useful for devices such as electrical switches, memories, image storage, and photo resistors. The common feature of these glasses is the presence of localized states in the mobility gap, as the result of the absence of long-range order as well as various inherent defects. Optical data storage based on laser induced amorphous to crystalline (a-c) phase transformation of chalcogenide glasses is an area with on-going research activity [2-9]. The trend of using amorphous semiconducting materials, rather than carefully prepared crystalline semiconductors, in electronic devices necessitates further investigation of such materials. These glasses are known to exhibit single glass transition and single crystallization temperatures, which is an important condition for rewritable disks. Several chalcogenide alloys have been developed as recording layer and their good practical performance has been reported [10–13].

Erasable recording is usually considered to be a potential replacement for conventional recording due to its high storage density and archival stability. The chalcogenides used for recording medium must be easy to amorphize and crystallize, and there should be a high optical contrast between the amorphous and crystalline states. In phase change technology (PC), the laser pulse of duration several hundred nanoseconds is used to erase a written spot. The a-c phase transformation in PC recording layer material must be very fast so as to enable erasing in such a short time. Hence, the study of ac phase transformation is of utmost importance for the development of some new chalcogenide glasses as better PC recording materials [14]. The addition of Bi to the Se-Te system is expected to modify the material properties to make it more suitable for reversible optical recording with an erase time less than 1 μsec. Thermal processes are known to be important in inducing crystallization in semiconducting chalcogenide glasses [15,16]. In order to view the suitability of a material for the above applications, it is necessary to investigate the crystallization behaviour of the material concerned.

In the present work, a systematic investigation of the crystallization kinetics of amorphous $Te_x(Bi_2Se_3)_{1-x}$ system has been made. The thermal stability and crystallization kinetics have been reported for the Te-Bi-Se system for different Te contents. In DTA two basic methods can be used, isothermal and non-isothermal. In the isothermal method, the sample is brought quickly to a temperature above the glass transition temperature (Tg) and the heat evolved during the crystallization process is recorded as a function of time while non isothermal method, the sample is heated at fixed rate and the heat evolved is recorded as a function of temperature or time. While isothermal experimental analysis techniques are more definite but non-isothermal thermo-analytical techniques have several advantages. The non-isothermal method has been used for the determination of the thermal stability of the amorphous alloys in the investigation of the processes of the nucleation and growth that occur during transformation of the metastable phases in the glassy alloys as it is heated. These techniques provide valuable information on such parameters, as the glass transition temperature, crystallization temperature and the activation energy, over a wide range of temperature [17]. Many phase transformations occur too rapidly to be measured under isothermal conditions because of transitions inherently associated with the experimental apparatus. Industrial processes often depend on the kinetic behavior of systems undergoing phase transformation under non-isothermal conditions. In this respect, a definitive measurement of non-isothermal transformation kinetic is desirable.

Calorimetric studies were made under non-isothermal conditions at different heating rates. The kinematical investigations are always connected with the concept of the activation energy. In glass crystallization phenomena, the values of these investigations are associated with the nucleation and growth processes, which dominate the devitrification of most glassy solids. In general, separate activation energies must be identified with individual nucleation and growth steps in a transformation, although they usually have been combined in to activation energy representative of the overall crystallization process. Selenium based melt are characterized by a high viscosity among amorphous chalcogenide alloys [18,19]. Selenium in particular has been reported to exhibit a unique property of reversible transformation, which makes these glasses useful as optical memory devices. It is reported [20,21] that addition of Te into a-Se results in dissociation of long polymeric chains and eight member rings of amorphous selenium . As a result Se-Te alloys are more important as compared to a-Se due to distinct advantages viz. greater hardness, better photosensitivity, lesser ageing effects etc. and hence find applications as recording layer material in optical phase change technique. However, limited reversibility and low glass transition and crystallization temperatures in these alloys are serious problems. These problems can be overcome by addition of third element as a chemical modifier as it is reported to expand the glass forming region and also creates compositional and configurational disorder [22]. This feature favours the glass formation in bulk form by air–quenching or water–quenching as well as in evaporated thin film forms. Since tellurium based melts with the same elements generally have low viscosity, a high cooling rate is required to prevent nucleation and growth during quenching and to obtain bulk glasses. The tellurium alloys have often been used for the active layer of those devices because of low melting point. Te-based alloys, which contain a small amount of As, Bi, Sb or Ge, exhibit fast crystallization processes after switching [23]. However, several problems like segregation and low crystallization temperature arises with these alloys. The segregation limits the reversible transition between amorphous and crystalline states, because the compositional deviation is likely to continue in the active layer in every crystallization process. The answer to the above problems may be a ternary solid alloy with relatively low melting point because no compositional changes occur in a solid solution when it is cycled between amorphous and crystalline states. In this paper, we report our studies on Te-Bi-Se ternary glasses with the variation in Te content. From the heating rate dependence of T_p, the activation energy for crystallization E_c has been evaluated.

MATERIALS AND METHODS

For the preparation of Te-Bi-Se glasses, high purity elements (99.999 %) in appropriate atomic percentage were weighed in to quartz ampoules. The ampoules, sealed under high vacuum conditions (10^{-5} Torr) were suspended in a vertical furnace at 900^oC for 24 hours, shaken vigorously for homogeneous mixing. The temperature was raised at a rate of 3 to 4 K/min. The melt was rapidly quenched in ice-water mixture. The quenched samples were removed from the ampoule by dissolving the ampoule in a mixture of $HF+H_2O_2$ for about 20 hours. The samples were then kept at room temperature in dark for about one month for attainment of thermodynamic equilibrium as stressed by Abkowitz in chalcogenide glasses [20]. Amorphous nature of the samples was ensured by the absence of any sharp peaks in the X-ray diffractograms.

The prepared solid solution in powder form has been used for thermal analysis using the Differential Thermal Analysis (DTA). This material was first sealed in a standard aluminium pan and the calorimetric thermo grams of various compositions of the samples were obtained with a RIGAKU DTA 8150 calorimeter in the temperature range 50-700^o C at various heating rates (10 – 20 ^oC min^{-1}). Calorimetric measurements were made under non-isothermal conditions and a multi-scan technique has been used for crystallization studies. The activation energy for crystallization (E_c) has been determined by using Kissinger's equation in different forms.

RESULTS AND DISCUSSION

In the Te-Bi-Se system the various bonds involved are Bi-Te, Bi-Se, Te-Se, Se-Se, Te-Te etc. The chemical bonds approach predicts that only three types of bonds, namely Bi-Te, Bi-Se and Se-Se bonds, are expected to form for the investigated compositions. In other words, the Te-Se, Te-Te and Bi-Bi bonds are not present. Addition of Bi leads to the formation of Bi-Se bonds at the expense of the Se-Se bonds. When the atomic percentage of Bi is increased in Te-Bi-Se glass system, Bi is expected to combine preferably with Se because the bond energy of Bi- Se (170.4 kJ/mol) is greater than that of Bi-Te (125.6 kJ/mol). This results in decreasing Se-Se bonds. The number of the Bi-Se bonds increases with increasing Bi content [24]. This explains the increase in T_g with the increase in Bi content due to the formation of large number of heteropolar Bi-Se bonds and decrease in homopolar Se-Se, Te-Te and Te-Se bonds. The results are similar to those obtained by earlier workers [25].

In memory devices using different electrical and optical properties in the crystalline and amorphous states, a lower melting point is preferable, because the crystalline state can be converted to the amorphous state by laser beam or electrical pulse with relatively lower energy. Moreover, those solids forming a solid solution are preferable, because phase separation or segregation does not occur in the transition from amorphous to crystalline state. The phase separation or segregation in crystallization processes cause degradation of memory devices. A higher crystallization temperature is also necessary for memory devices.

It is well known that thermal relaxation occurs in a glassy substance following an instantaneous change in temperature, during the quenching process, as it relaxes from a state of higher enthalpy towards a metastable equilibrium state of lower enthalpy. This type of thermal relaxation depends upon the annealing temperature and may be quite fast near the glass transition temperature. The glass transition is exhibited in Differential Thermal Analysis or Differential Scanning Calorimeter traces as an endothermic peak or a shift in the base line due to a change in specific heat. However, in chalcogenide glasses, such an endothermic peak can also be observed due to a fast change in enthalpy when the glassy system relaxes quickly due to a decrease in viscosity at the glass transition temperature. DTA or DSC techniques can, therefore, be quite useful in the study of thermal relaxation in glasses.

Among chalcogenide glasses, Se-Te based alloys have gained much importance because of their higher photosensitivity, greater hardness, higher crystallization temperature, and smaller ageing effects as compared to pure Se glass. A typical DTA curve for Te at 30% with heating rate of 10 K/min is shown in Fig. 1. The single endothermic glass transition peak indicates the homogeneity of the glass. Fig (2) shows the variation of T_p with Te content at different heating rates ranging from 10 K/min to 20 K/min. It is deduced from the figure that the value of T_p increases with the increase in Te content whereas it is found to be increasing with the increase in heating rates from 10 K/min to 20 K/min.

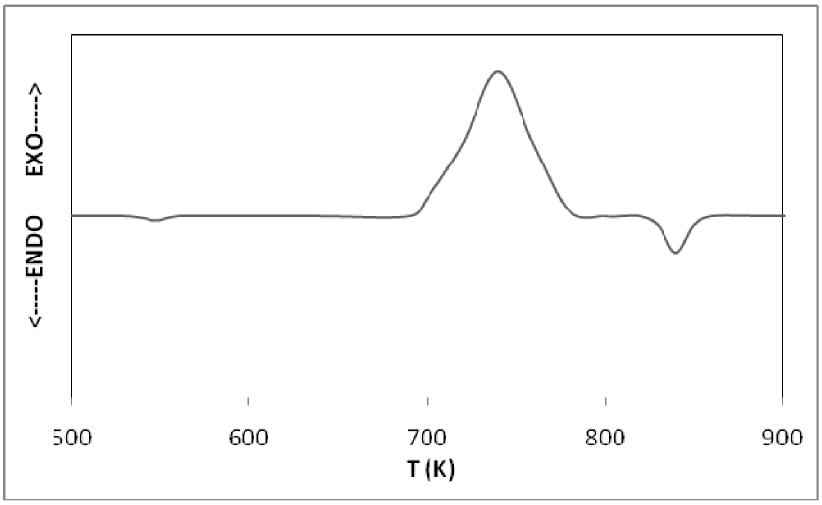

Fig 1 : DTA curves for Te at 30% for different heating rates.

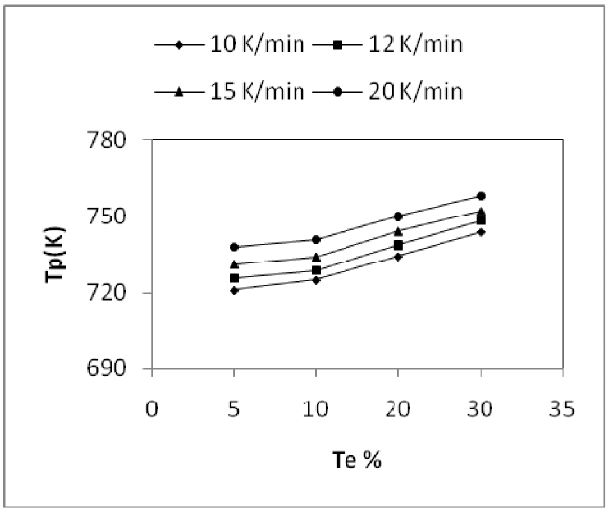

Fig 2 : Variation of T_p with Te content at various heating rates.

Theoretical aspects for calculating E_c

The activation energies to be considered in a crystalline process are the activation energy for nucleation (E_n), activation energy for crystal growth (E_g) and that for the whole process of crystallization, called the activation energy for crystallization, denoted by E_c. The thermal analysis methods enable the determination of E_c [26,27]. It has been pointed out that in non-isothermal measurements, generally due to a rapid temperature rise and big differences in the latent heats of nucleation and growth of the crystalline phase from the amorphous matrix; nucleation is more or less calorimetrically unobservable at temperatures below the crystallisation exotherm, or it takes place very rapidly and immediately after overheating of the material in the initial stages of the crystallisation exotherm, which results in the deformed beginning of the measured exotherm [28].

Based on the experimental results, the theoretical approach is set up on three models to exhibit how the activation energy associated with crystallization is modified with respect to the different parameters.

First Model - The activation energy, E_c, of the amorphous to crystalline transformation is calculated by using the equation derived by Kissinger [29,30]

$$\ln (T_p^2/\beta) = (E_c/kT_p) + \text{constant} \qquad \{1\}$$

Fig. (3) shows the relations between ln (T_p^2/β) and $10^3/T_p$ for different compositions of Te-Bi-Se system. The data are well fitted by straight lines, which show that the crystallization obeys the above-mentioned relation. It is evident from the fig. (6) that the value of activation energy, E_c increases from 1.865 eV to 2.170 eV with the increase in Te content, using the relation (1), for Te-Bi-Se system.

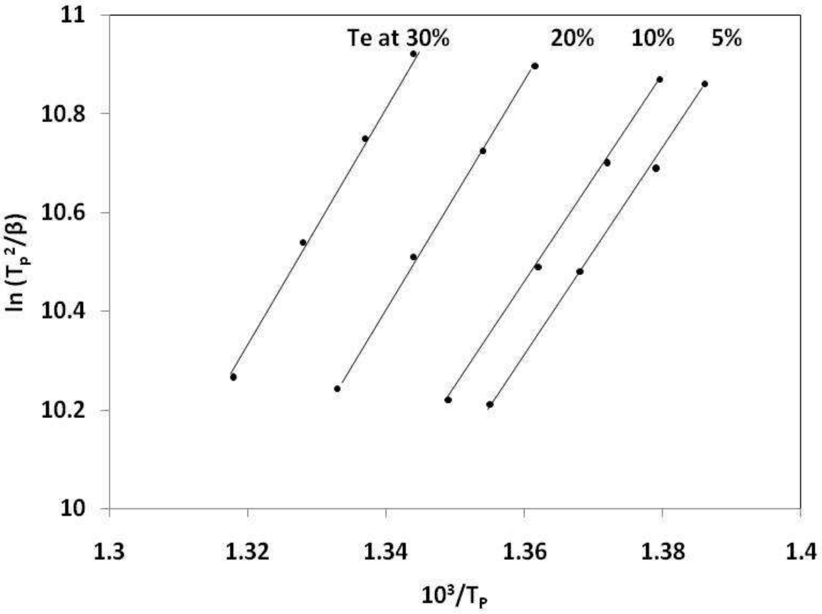

Fig.3 : Relation between ln (T_p^2/β) and $10^3/T_p$ for various compositions.

Second Model - The activation energy of the amorphous to crystalline transformation, E_c, can be calculated also from the following relation, which correlate the shifts in T_p values of DTA with the heating rate [29,31].

$$\ln \beta = - E_c/kT_p + \text{constant} \qquad \{2\}$$

Fig (4) shows the plots of lnβ with $10^3/T_p$ for Te-Bi-Se glass system. The data are well fitted by straight lines, which show that the crystallization obeys the above-mentioned relation (2). The values of E_c are found to increase from 1.826 eV to 2.185 eV with the increase in Te content using the relation (2) as shown in Fig (6).

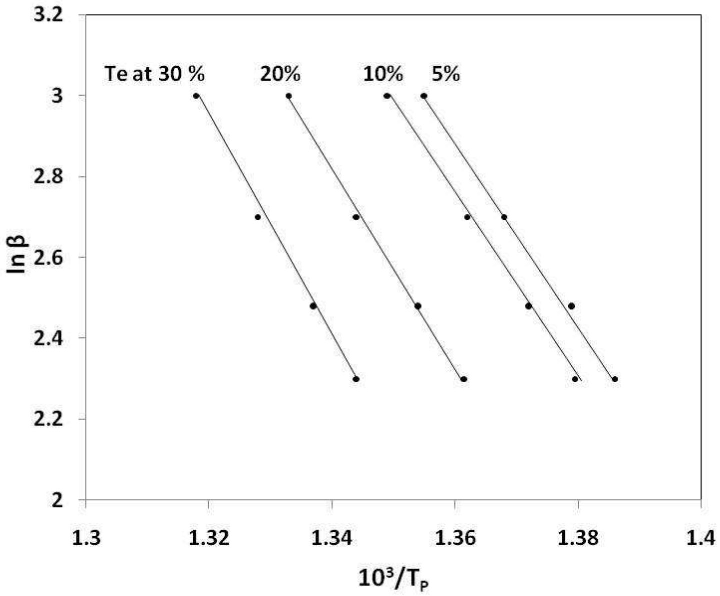

Fig 4: Relation between ln β and 10^3/ T_p for various compositions.

Third Model - The third model, used to calculate the values of E_c, is based on Marseglia's theory [32,33], which admits that

$$\ln T_p/\beta = E_c/kT_p + \text{constant} \qquad \{3\}$$

Plots of ln T_p/β versus $10^3/T_p$ for different compositions of Te-Bi-Se glass system are shown in fig (5). A straight line could be fitted to give the activation energies, which are listed in table 2. The values of E_c, obtained by using relation (3), are also shown in fig (6) with the variation of Te content. It is clear from the fig (6) that the value of E_c increases from 1.868 eV to 2.227 eV with the increase in Te content of Te-Bi-Se system. For all the three relations, the E_c increases with increase in Te content. It is found that the values of E_c, obtained using these relations, are almost same.

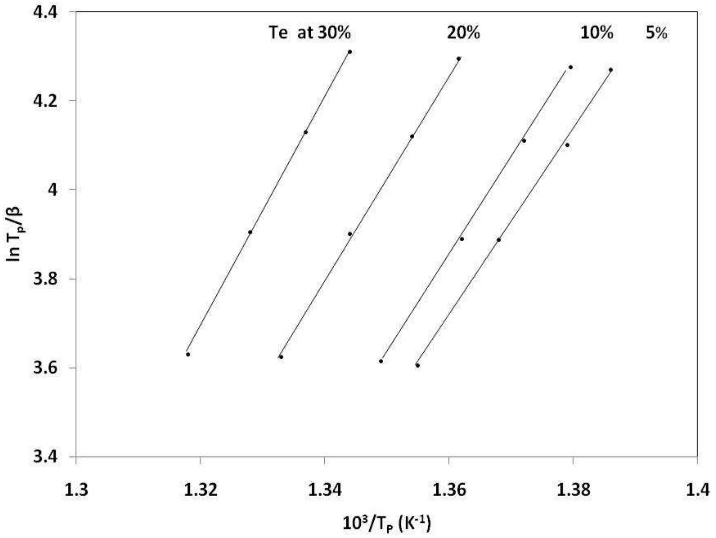

Fig 5 : Relation between ln (T_p/β) and 10^3/ T_p for various compositions.

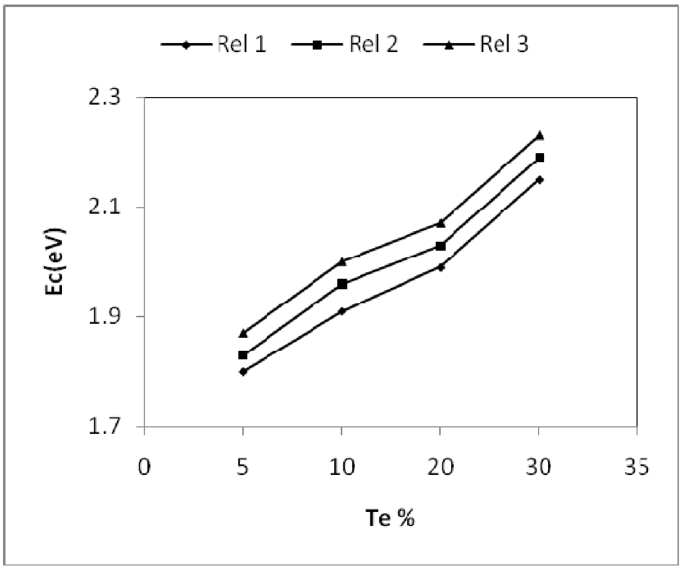

Fig 6 : Ec with variation of Te for Relations (1,2,3).

CONCLUSION

The effect of varying the concentration of Te in Te-Bi-Se alloys on the crystallization kinetics and activation energy has been investigated. It is found that the glass transition temperature shows little variation with the addition of Te. The value of peak of crystallization T_p is found to increase with the increase in Te content. From the heating rate dependence of T_p the activation energy for the crystallization has been evaluated. The results are discussed on the basis of Kissinger's approach and Marseglia's theory for non-isothermal crystallization. The activation energy E_c, calculated using all the three approaches (1,2,3), increases with increase in Te content. There is not much difference between the obtained values of E_c, so it can be concluded that any of these models can be taken to calculate E_c as the values of activation energies, using three different models, are in good agreement with each other.

REFERENCES

[1] S. A. Khan, F.S. Al-Hazmi, A.S. Faidah, A.A. Al-Ghamdi, *Current Applied Physics*, **2009**, 9, 567.
[2] M. Nakamura, Y. Wang, O. Matsuda, K. Inoue, K. Murase, *J. Non-Cryst. Sol.*, **1996**, 740 198.
[3] L. Men, F. Jiang, F. Gan, *Mater. Sci. Eng.*, **1997**, B 47, 18.
[4] R. V. Woudenberg, *Jpn. J. Appl. Phys.*, **1998**, 37, 2159.
[5] T. Babeva, D. Dimitrov, S. Kitova, I. Konstantinov, *Vacuum*, **2000**, 58, 496.
[6] V. I. Mikla, I. P. Mikhalko, V.V. Mikla, *Mater. Sci. Eng.*, **2001**, B 83, 74.
[7] A. S. Maan, D. R. Goyal, *Chalcogenide Letters*, **2007**, 4(8), 89.
[8] A. K. Kolobov, J. Tominaga, *J. Optoelectron. Adv. Mater.*, **2002**, 4 (3), 679.
[9] S. A. Khan, M. Zulfequar, M. Husain, *Vacuum*, **2003**, 72, 291.
[10] L. H. Chou, Y. Y. Chang, Y. C. Chai, S. Y. Wang, *J. Appl. Phys. Part 1*, **2001**, 40(8), 4924.
[11] J. Li, L. Hou, H. Raun, Q. Xie, F. Gan, *Proceedings SPIE - Int. Soc. Opt. Eng.*, **2001**, **125**, 4085.

[12] T. Wagner, M. Frumar, S. O. Kasap, Mir. Vlcek, Mil. Vlcek, *J. Optoelectron. Adv. Mater.*, **2001**, 3(2), 227.
[13] J. Gutwirth, T. Wagner, T. Kohoutek, Mir. Vlcek, S. Schroeter, V. Kovanda, Mil. Vlcek, M.Frumar, *J. Optoelectron. Adv. Mater*., **2003**, 5 (5) 1139.
[14] Y. Sripathi, G.B. Reddy and L. K. Malhotra, *J Mater.Sci.: Mater. in Elec.*, **1992**, 3,164.
[15] A. A. Abu-Sehly, *J Mater. Sci*., **2000**, 35, 2009.
[16] R. K. Quinn and R. T. Jhonson, *J Non-Crystalline Solids,* 1**972**, 7, 53.
[17] D.W. Henderson, *J Non-Crystalline Solids,* **1979**, 30, 301.
[18] Z. H. Khan, M. Zulfequar and M. Husain, *J. Mod. Opt*., **1997**, 44, 55.
[19] M. Ilyas, M. Zulfequar and M. Husain, *Optical Materials*, **2000**, 13, 397.
[20] M. A. Abkowitz in '"*The Physics of Se and Te*" edited by E. Gerlach, P. Grosse (Springer, Berlin, **1979**) 178.
[21] M. F. Kotakata, M. K. El-Mously, *Acta Physica Hungarica,* **1983**, 54(3), 303.
[22] Z. H. Khan, M. Zulfequar, M. Illyas, M. Hussain, Kh. Selima Begum, *Current Appl. Phys*. **2002**, 2, 164.
[23] M. Saxena and P. K. Bhatnagar, *Bull. Mater. Sci.*, **2003**, 26, 547.
[24] O. El-Shazly and M. M. Hafiz, *J Mater.Sci.: Mater. in Electronics*, **2001**, 12, 395.
[25] S. Rahman, M. V. Ramana and G. S. Sastry, *J. Mater. Sci. Lett*., **1991**, 10, 192.
[26] S. Ranganathan and M. V. Heimendahl, *J Mater. Sci*., **1981**, 16, 2401.
[27] M. V. Heimendahl and G. Kuuglstatter, *J Mater. Sci.,* **1981**, 16, 2405.
[28] E. Illekova, *J. Non-Crystalline Solids*, **1984**, 68, 153.
[29] M.A. Abdel - Rahim, *J. Mater. Sci*., **1992**, 27, 1757.
[30] H. E. Kissinger, *Anal. Chem.*, **1957**, 29, 1702.
[31] S. Mahadevan, A. Giridhar and A.K. Singh, *J. Non-Crystalline Solids,* **1986**, 88, 11.
[32] E. A. Marseglia, *J. Non-Crystalline Solids*, **1980**, 41, 31.
[33] H. Atmani, *Mater. Chem. and Phys*., **1988**, 19, 255.