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Kinetics of First Order Phase Transformation in $Se_{75}Te_{19}In_6$ Glass for Phase Change Memory

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Abstract

In the present research work, we have studied the kinetics of first order phase transformation in $Se_{75}Te_{19}In_6$ glass synthesized by melt quenching technique. The amorphous nature of the synthesized sample was confirmed by High Resolution X-Ray Diffraction (HRXRD). The kinetics study during phase transformation were studied by Differential Scanning Calorimetry (DSC) under non-isothermal conditions at various heating rates 5, 10, 15, 20 and 25K/min. The values of kinetics parameters such as glass transition (T_g), on-set crystallization (T_c), peak crystallization (T_p) and melting temperature (T_m) were determined with the help of DSC thermograms. The activation energies of crystallization (ΔE_c) and structural relaxation (ΔE_t) were calculated by using Kissinger, Ozawa and Moynihan approaches and found to be in good agreement to each other.

Keywords: Activation energy, Chalcogenide glass, Crystallization, DSC, HRXRD.

1. Introduction

Chalcogenide glasses have great significance and extensively investigated in past decades for their numerous excellent and exclusive physical, optical, electrical and thermal properties. These unique glasses have grown as a very popular family of inorganic glassy materials containing chalcogen elements (S, Se and Te) in optimum combination with other elements (Zn, Sb, Sn, In, Ag etc.) of the periodic table for the fabrication of applicable devices in various fields**.** They have found use in a variety of applications due to their better I-R transmission, small photo energy, and high value of refractive index [1]-[2]. The short range ordered structure of these distinctive class of glasses make them flexible and facilitate to

easily tailored them with other materials and so an optimum composition may be used in various fields for different applications such as photo-resistor, IR Lenses, thermal imaging, Xerography, IR detector, laser, solar cell, optical fibers, diffractive waveguides, biosensors, frequency converters, optical amplifiers etc. [3-6]. Their optical high non linearity makes them suitable for all-optical switching [7]. The crystalline and amorphous states of these glasses have dramatically different physical properties. The inimitable property of reversible transformation between these two states makes them compatible for phase change memory material [8]. These unique glasses are attuned for chemical sensors, since the vibrations of the maximum molecular species lie in the infra-red portion of electromagnetic spectrum [9]. They are also predicted as a new family of potential high-performance thermoelectric materials. A recent proposed application of these materials is as radiation sensors for nuclear wastes. The chalcogenides glasses have a great possibility as multifunctional optoelectronic material for the future evolving uses and for much efficient solar energy collection. Chalcogenides in thin film form are high performance and cheaper photovoltaic solar cell materials than silica or other photovoltaic solar cell materials.

To make these distinctive glasses useful in various usages it is desirable to study their first order phase transformation kinetics. The crystallization kinetics in chalcogenide glasses plays a very important role in defining thermal stability, transport mechanism, glass forming ability etc. The study of kinetics during crystallization provides the information about the durability of glassy devices. Differential Scanning Calorimetry (DSC) is much popular techniques for kinetics study in glassy systems. It is extensively used to examine glass transition and crystallization kinetics due to small amount requirement of sample, its rapidity, easier approach and sensitivity. DSC studies may be examined under two conditions, isothermal and non-isothermal. In the isothermal method the sample is carried quickly to a temperature above the glass transition temperature and grown heat at a constant temperature is recorded with respect to time during the crystallization process. The isothermal condition is not a convenient and practical method due to difficulty of attaining a homogeneous temperature of the furnace during the whole crystallization kinetics process. In non-isothermal one the sample is heated with a constant heating rate and produced heat is recorded as a function of temperature. This condition is generally adopted by the workers due to broader temperature range and much easier approach.

Many authors have studied the kinetics of first order phase transformation in chalcogenide materials using DSC (non-isothermal conditions). The Johnson-Mehl-Avrami (JMA) [10-12]

model provides the basis for crystallization kinetics theory designed basically for isothermal condition but also valid for non-isothermal condition under certain limits. Several workers have applied different approaches on the basis of JMA Model [13-18] of crystallization via nucleation and growth under non-isothermal condition. Dahshan et al. [13] have studied the crystallization kinetics in Ge-Se-Sb-Ag glass. Wagner et. Al [14] have done the analysis of crystallization kinetics in Cu-As-Te glasses. Soltan et al. [15] has examined the DSC data of Se-Te-Sb glasses under non-isothermal condition and evaluated the glass transition temperature and fragility index. Sherchenkov et al. [16] have studied the crystallization kinetics of $Ge_2Sb_2Te_5$ (doped with Bi). Svoboda et al. [17] have discussed the crystallization kinetics in Se–Te glassy system. Imran [18] has studied the glass transition kinetics, crystallization kinetics and thermal stability of $Se_{70-x}Ga_{30}In_x$ glass. Heireche et al. [19] have discussed about the crystallization kinetic study of $Se_{90-x}In_{10}Sb_x$ glass. The work on glass transition kinetics analysis of Sb-Se-Ge has been done by Sharda et al. [20].The kinetics of glass transition and physical ageing of Ge-Se glasses has been done by Zhao et al. [21]. Non-isothermal crystallization kinetics of $Se_{90-x}Zn_{10}Sb_x$ glasses has been investigated by Heireche el. Al. [22]. The investigation of crystallization kinetics in glassy Se and binary $Se_{98}M_2$ (M=Ag, Cd, Zn) has been done by Chandrabhan et al. [23]. The study of crystallization behavior of chalcogenide alloys by Khan et al. [24]-26] is worth mentioning.

In this research work, we have used Selenium (Se) as a parent material for the composition due to its unique property of reversible phase transformation which makes this an appropriate material for optical recording devices. Se has also great photoconductive and photovoltaic properties and these are quiet beneficial in photocopying, photocells and solar cells. Unfortunately Se has some inferior parameters such as ageing effect, lower sensitivity, and thermal instability. Several efforts have been done to modify these parameters by tailoring them with metals. Se-Te based glasses are believed to be one of the best capable media for phase change devices. Te improves the crystallanity and corrosion resistance of Se. Te alloys have often used for the active layer of memory devices because of their lower melting point [27]. Indium (In) is doped with the Se-Te composition as it is a post transition, very soft, malleable, easily fusible metal and exhibit photovoltaic effect and most attuned for solar cell. Addition of In concentration in binary alloy Se-Te changed the chemical equilibrium of existing bonds, so the newly made ternary alloy stoichiometry would heavily crossed –link and makes new homopolar and hetropolar bonds in respect of alloying elements.

2. Experimental Details

Rapid melt quenching technique was used to prepare $Se_{75}Te_{19}In_6$ chalcogenide glass. High purity materials from Sigma Al-drich (5N purity) with proper atomic percentage were weighed and packed up in a clean evacuated quartz ampoule to avoid oxidation of the sample. The ampoule was kept inside a furnace at 1373 K temperature for 11 h. For realizing the homogeneity of the composition the ampoule was continuously shaken. The melt was immediately quenched into ice-cooled water to obtain the desired glass. The material ingot was crushed into powdered form using pastel and mortal set. The amorphous nature of the synthesized sample was confirmed by High Resolution X-Ray Differactometric (HRXRD) study using Regaku X-Ray differactometer Ultima IV). The 10 mg of powdered samples crimped in Aluminium (Al) pan were scanned at heating rates of rates 5, 10, 15, 20 and 25K/min using DSC (model DSC plus, Reheometric Scientific Company, UK) under air atmosphere. The Al pan was with flat bottom ensuring good thermal contact between sample and pan and inert to reactive with sample. We have prior calibrated the DSC instrument before measurements with the help of standard materials Pb, In with known melting points. The values of glass transition (T_g), onset crystallization (T_c), peak crystallization (T_p) and melting temperature (T_m) were evaluated by DSC curves using microprocessor of the thermal analyzer. The powdered sample of $Se_{75}Te_{19}In_6$ was crystallized by placing the sample in a vacuum muffle furnace at 365 K (which is near the T_c of the sample) for 2 hours. The transformation of phase in annealed $Se_{75}Te_{19}In_6$ glass was confirmed by HRXRD studies.

3. Results and Discussions

The kinetics of first order phase transformation of any material can be characterized by its endothermic and exothermic peaks of DSC curve. Typical DSC traces of $Se_{75}Te_{19}In_6$ obtained at heating rates 5, 10, 15 and 20 K/min are presented in Fig.1.

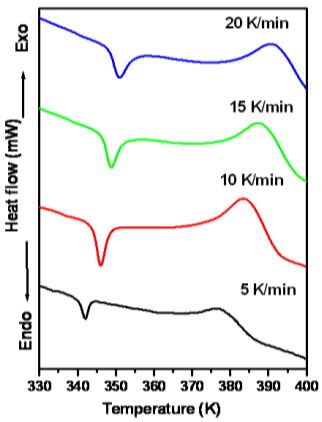

Fig. 1

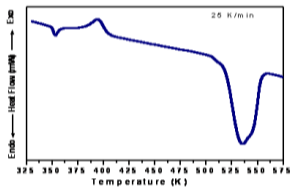

Fig. 2

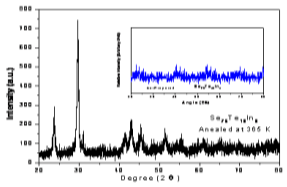

Fig. 3

Fig. 1-3: DSC and XRD of the Compound.

Two characteristic phenomenon are appear in DSC curve, the first one is glass transition temperature (T_g) which is temperature at which glass starts softening directed that at this temperature they becomes more viscous. Glass transition is usually not a thermodynamics phenomenon, but a temperature range over which the mobility of molecular chain increases significantly. At glass transition temperature (T_g) specific heat, coefficient of thermal expansion and free volume of the sample changes abruptly. The exothermic peaks are the crystallization temperature (T_c) of the glassy alloy at which all the molecules are arranged in regular structure.. Fig. 2 represents the DSC curve at heating rate 25 K/min in which third endothermic peak is observed which refer to the melting temperature T_m (found to be 536 K) and reveals the extent of energy which release owing to whole extinguish of the solid phase structure cause breaking of all type of present bonds in solid alloy**.** Table-1 shows the values of T_g, T_c and T_p at different heating rates. We can see that there is a significant increase in glass transition and crystallization temperature with increasing heating rate. The shift of T_g can be explained by its theoretical definition that T_g is the temperature at which relaxation time τ and relaxation time of observation τ_{obs} both are exactly equal. T_g depends reciprocally on relaxation time and τ_{obs} rises with heating rate. So evidently T_g increases with increase in heating rate. The swing of T_c to the higher temperatures with heating rate can be ascribed to the fact that when heating rate is raised, the system does not acquire enough time for nucleation and crystallization. By the time crystallization starts taking place, the temperature goes up owing to the higher heating rates. The XRD pattern of as-prepared sample is represented in the inset of Fig. 3. The absence of any sharp structural peaks confirms the amorphous nature of the sample. Fig. 3 shows the HRXRD PATTERN OF crystallized sample at 365 K for two hours. The presence of sharp structural peaks confirms the crystalline nature of the sample. The crystallized peaks found in diffraction pattern at diffraction angles 24^0, 29^0, 43^0, 45^0 and 51^0 which ensure structural transformation from amorphous to crystalline state of the sample.

The activation energy (ΔE_c) of crystallization is the extent of energy which needs to initiate the glassy to crystalline phase. On the basis of most reliable JMA crystallization theory two approaches were used for the determination of ΔE_c. The first one is Kissinger [28] approach and the other is Ozawa [29] approach.

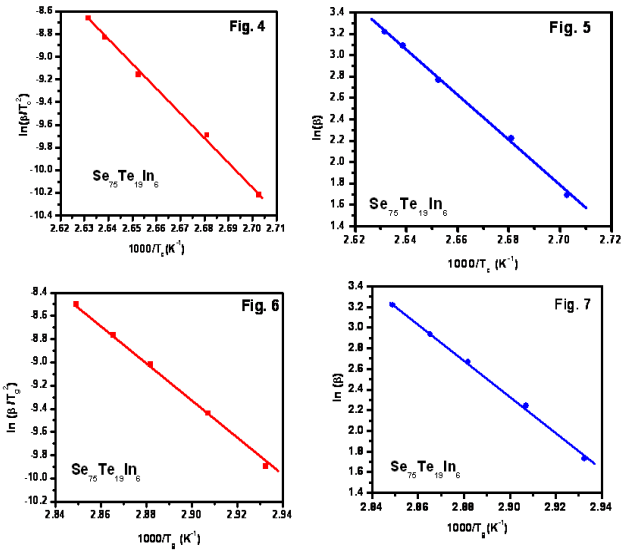

Fig. 4-7: Variation of $\ln(\beta/T_c^2)$ with 1000/T

The Kissinger approach is given by

$$\ln (\beta/T_c^2) = \text{constant}-(\Delta E_c/RT_c) \qquad (1)$$

Where β represents heating rate and R is Rydberg constant.

A plot of $\ln(\beta/T_c^2)$ vs $1000/T_c$ is shown in Fig. 4, whose linearity indicates that results justify the Kissinger formula**.** Using the slope of this plot ΔE_c has been calculated and is given in Table-1 and found to be 177.96kcal/mol.

The Ozawa approach is given by

$$\ln\beta = \text{constant}-(\Delta E_c/RT_c) \qquad (2)$$

A plot of $\ln\beta$ vs $1000/T_c$ is shown in Fig.5. This graph is found to be linear. From the slope of this graph we have determined the value of ΔE_c (shown in Table-1) and found to be 174.57 kcal/mol. There is good agreement between these two approaches. The average of ΔE_c is 176.27 kcal/mol.

Glass transition studies are essential for understanding the mechanism of glass transformations and to estimate the structural rigidity of the glasses. The activation energy of structural relaxation (ΔE_t) depends on the molecular movements and their reorganizations and can be evaluated using the values of heating rate (β) with the corresponding glass transition temperature (T_g) by using two different equations from Kissinger [28] and Moynihan et al.[30] approach.

According to Kissinger approach

$$\ln (\beta/T_g^2) = (\text{constant}) - (\Delta E_t/RT_g) \qquad (3)$$

It is evident from this equation that the plots of $1000/T_g$ vs. $\ln(\beta/T_g^2)$ should be straight line (shown in Fig. 6). The value of ΔE_t has been calculated from the slope of this graph and listed in Table-1 and found to be 138.02 kcal/mol.

The heating rate (β) dependence of T_g in chalcogenide glass may be interpreted in term of thermal relaxation phenomena and it is shown by Moynihan et al. [30] that ΔE_t can be related to β and T_g by the relation

$$\ln \beta = (\text{constant}) - (\Delta E_t / RT_g) \qquad (4)$$

It is clear from this equation that the plot of $1000/T_g$ vs $\ln\beta$ should be straight line (Shown in Fig. 7) and the value of ΔE_t has been calculated from the slope of this graph (listed in Table-1) and found to be 146.75kcal/mol.

It may be noted from Table-1 that values of activation energies of structural relaxation (ΔE_t) calculated from two approaches are in good agreement to each other. The average value of ΔE_t is 142.39kcal/mol.

4. Conclusions

The kinetics of first order phase transformation in $Se_{75}Te_{19}In_6$ glass were studied and discussed. The shift in T_g and T_c with heating rate attributed to the relaxation time of observation and induction time respectively. The activation energy of the crystallization and glass transition were determined from the heating rate dependence of the glass transition temperature, by employing Kissinger, Ozawa and Moynihan approaches. HRXRD observations showed that crystallized sample is in crystalline phase which confirms the phase transformation in glassy system. A comprehensive study of kinetics of first order phase transformation in $Se_{75}Te_{19}In_6$ glass is very significant to use of this material for more innovative devices in various fields of interest depending on transformations from amorphous to crystallization phase.

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6. References

1. M. L. Anne, J. Keirsse,V. Nazabai, K. Hyodo, S. Inoue, C.B. Pledel ,H. Lhermite , J. Charrier , K. Yanakata, O. Loreal, J.L. Person, F. Colas, C. Compere, and B. Bereau, Chalcogenide glass optical waveguide for infrared biosensing, Sensors, Vol. 9, pp. 7398-7411, 2009.
2. J. S.Sanghera, L. B. Shaw, and I. D. Aggarwal, Applications of chalcogenide glass, Comptes Rendus Chimieoptical fibers, Vol. 5, pp. 873-883, 2002.
3. S John. et. al, Pierce Infrared-transparent glass ceramics: An exploratory study, J..Non-Cryst. Solids, Vol. 410 (15) pp. 160-173, 2015.
4. L Le Neindre., F. Smektala, K. Le Foulgoc, X. H. Zhang, and J. Lucas, Tellurium Halide Optical Fibers, J. Non-Cryst. Solids, Vol. 242, pp. 299-103, 1998.
5. K. Teodor, Todorov, Jiang Tang, Santanu Bag, Oki Gunawan, Tayfun Gokmen, Yu Zhu, and David B. Mitzi, Beyond 11% Efficiency: Characteristics of State-of-the-Art Cu2ZnSn(S,Se) 4 Solar cells, Advanced energy materials. Vol. 3(1), pp. 34-38, 2013.
6. M. Hughes, W. Yang, and D. Hewak, Fabrication and characterization of femtosecond laser written waveguides in chalcogenide glasses, Appl. Physics. Lett, Vol. 90(13), 131113-1 to-3, 2007.
7. M. Jeffrey, F. O. IIday, F. W. Wise, and B. G. Aitken, Highly nonlinear Ge-As-Se and Ge-As-S-Se glasses for All optical switching, IEEE Photonics Tech, Lett., Vol. 14. pp. 822-824, 2002.
8. S. R. Ovshinisky, and H. Fritzsche." Amorphous semiconductors for switching memory and imaging application", IEEE Trans. Electron. Vol. 20(2), pp. 91-105, 1973.
9. M. Miloshova, D. Baltes and E. Bychkov, New chalcogenide glass chemical sensors for S2- and dissolved H2S monitoring, 47(2), 135-40, 2003.
10. W. A. Johnson, R. F. Mehl, Reaction kinetics in processes of nucleation and growth, Trans Am Inst Min (Metal) Eng, 1939; 135, 416–60, 1939.
11. M. Avrami, Kinetics of phase change II. Transformation time relations for random distribution of nuclei, J Phys Chem, 8(2), 212–24, 1940.
12. M. Avrami, Kinetics of phase change I, general theory, J Phys Chem, 7(12), 1103–12, 1939.
13. A. Dahshan, Crystallization kinetics of new Ge20Se60Sb20−xAgx ($0 \leq x \leq 20$ at. %) glasses, J.All. Compds, 670, 306-311, 2016.

14. C. Wagner, J. Vhzquez, M. Dominguez, P. Villares, and R. Jimhez-Garay, Analysis of the crystallization kinetics in the semiconducting glassy alloy $Cu_{0.20}As_{0.35}Te_{0.45}$, Materials Chemistry and Physics, 43, 227-232, 1996.
15. A.S. Soltan, A.A. Abu-Sehly, A.A. Joraid, and S.N. Alamri, The activation energy and fragility index of the glass transition in $Se_{76}Te_{21}Sb_3$ chalcogenide glass, Thermochimica Acta, 574, 73-78, 2013.
16. A. Sherchenkov, S. Kozyukhin, A. Babich, and P. Lazarenko, Thermal properties of phase change material $Ge_2Sb_2Te_5$ doped with Bi, J Non-Cryst Solids, 377, 26-29, 2013.
17. Roman Svoboda, Miloš Krbal, and Jiří Málek, Crystallization kinetics in Se–Te glassy system, J. Non-Cryst. Solids, 357(16–17), 3123-3129, 2011.
18. Mousa M.A. Imran, Crystallization kinetics, glass transition kinetics, and thermal stability of $Se_{70-x}Ga_{30}In_x$ (x=5, 10, 15, and 20) semiconducting glasses, Physica B: Condensed Matter, 406(3), 482-487, 2011.
19. M. M. Heireche, Non-isothermal crystallisation kinetics study on $Se_{90-x}In_{10}Sb_x$ (x = 0, 1, 2, 4, 5) chalcogenide glasses, J. Ther. Anal. Cal., 114(1), 195–203, 2013.
20. Sunanda Sharda, Neha Sharma, Pankaj Sharma, and Vineet Sharma, Glass transition and crystallization kinetics analysis of Sb–Se–Ge chalcogenide glasses, J. Ther. Anal. Cal., 115(1), 361–366 , 2014
21. H.Y. Zhao, Y.P. Koh, M. Pyda, S. Sen, and S.L. Simon, The kinetics of the glass transition and physical aging in germanium selenide glasses, J. Non-Cryst. Solids, 368, 63-70, 2013.
22. Lamia Heireche, Mohamed Heireche, and Maamar Belhadji, Kinetic Study of Non-IsothermalCrystallization in $Se_{90-x}Zn_{10}Sb_x$ (x = 0, 2, 4, 6) Chalcogenide Glasses, J. Cryst. Proc.Tech., 4, 111-120, 2014.
23. Chandrabhan Dohare, and Neeraj Mehta, Investigation of Crystallization Kinetics in Glassy Se and Binary $Se_{98}M_2$ (M = Ag, Cd, Zn) Alloys Using DSC Technique in Non-Isothermal Mode, J. Cryst. Proc. Tech., 2, 167-174, 2012.
24. Shamshad A. Khan, J.K. Lal, F.A. Al-Agel, and M.A. Alvi, Non-isothermal crystallization in Ga–Se–Ag chalcogenide glass by differential scanning calorimetry, J. All. Comp. 554, 227-231, 2013.
25. Shamshad A. Khan, F.S. Al-Hazmi, A.S. Faidah, and A.A. Al-Ghamdi Calorimetric studies of the crystallization process in a-Se75S25−xAgx chalcogenide glasses, Current Applied Physics. 9(3), 567-572, 2009.

26. Shamshad A. Khan, Zishan H. Khan, M. Zulfequar, and M. Husain, Kinetics study of a-Se80Te20−xPbx using non-isothermal crystallization, Physica B: Condensed Matter, 400(1–2), 180-184, 2007.
27. Tung-Hua Chuang, Yi Chou Chen, Tsung-Shune Chin, Kin-Fu Kao, Po-Chin Chang, and Yung-Ching Chu, Quarternary Gallium Tellurium Antimony (M-GaTeSb) Based Phase Change Memory Devices, Macronics International Co. Ltd. AH01L4500FI 257 2, 2012.
28. H. E. Kissinger, Reaction Kinetics in Differential Thermal Analy. Anal. Chem., 29, 1702-1706, 1957.
29. T. Ozawa, Kinetics of non-isothermal crystallization, Polymer, 12, 150-158, 1971.
30. C. T. Moynihan, A. J. Easteal, and J. Wilder, J. Tucker, Dependence of the glass transition temperature on heating and cooling rate, J. Physics. Chem, 78, 2673-2677, 1974.

Table 1

Different crystallization parameters of $Se_{75}Te_{19}In_6$ during non-isothermal DSC measurements

Crys. Parameters	Heating Rate (β) (K/min)				
	5	10	15	20	25
T_g (K)	341	344	347	349	350
T_c (K)	370	373	377	379	380
T_p (K)	377	384	389	392	395
The activation energy of structural relaxation and crystallization					
ΔE_c (kcal/mol)			ΔE_t (kcal/mol)		
Kissinger Approach	Ozawa Approach		Kissinger Approach	Moynihan Approach	
177.96	174.57		138.02	146.75	