International Journal of New Horizons in Physics

http://dx.doi.org/10.12785/ijnhp/020205

Thermal Analysis of Quaternary Ge-As-Te-Sn Glasses

M. A Abousehly[1], *A.M. Abd Elnaeim*[1], *K. A. Aly* [1,2,*] *and A. Dahshan*[3,4].

[1]Physics Department, faculty of science, Al -Azhar University, Assiut, Egypt.
[2]Physics Department, Faculty of Science and Arts, Jeddah University (KAU), P.O. Box 80200, 21589 Khulais, Saudi Arabia.
[3]Department of Physics, Faculty of Science, Port Said, University, Port Said, Egypt.
[4]Department of Physics - Faculty of Girls - King Khalid University Abha, Saudi Arabia.

Received: 21 Feb. 2015, Revised: 22 Mar. 2015, Accepted: 24 Mar. 2015.

Abstract: The results of Differential Scanning Calorimetry (DSC) under non-isothermal conditions on chalcogenide $Ge_{12}As_{23}Te_{65-x}Sn_x$ (x = 0, 2 and 4 at. %) glasses were reported and discussed. The dependence of the characteristic temperatures (glass transition temperature (T_g), the crystallization onset temperature (T_c) and the crystallization peak temperature (T_p)) on the heating rate (β) has been utilized to determine the activation energy for the glass transition (E_g), the activation energy for crystallization (E_c) and the Avrami's exponent. Furthermore, the obtained results were discussed in terms of the chemical bond approach, the average heat of atomization and the cohesive energy (CE).

Keywords: Glassy alloy, Non-isothermal process, Glass transition, Crystallization kinetics, crystalline phases.

1 Introduction

Chalcogenide glasses have been studied intensively in the last few decades because their interesting properties and possible technological applications [1,2]. The physical properties of these glasses are usually affected by the addition of impurities as a third or fourth element. Recently, a lot of attention has been paid to the influence of impurities on both the electrical, and the optical properties as well as the thermal analysis of their glasses. The strong influence of small quantities of Ga, In, Ag, Cu on the electrical properties of As_2Se_3 was pointed out by Kolomiets [3-5]. Recently, A. Othman have study the effect of Te additions on the optical [6], photoelectrical properties [7], and the thermal analysis [8] of some As-Sb-Se chalcogenide glasses.

It is also important to understand the crystallization kinetics in chalcogenide glasses for the manufacturing of glass-ceramics and to prevent devitrification. Differential scanning calorimetry (DSC) is valuable for the quantitative study of crystallization in different glassy systems. Such studies have been widely discussed in the literature [9-14] [5-11]. There are different methods and theoretical models [15,16] [12–14] were proposed to get crystallization kinetics by using the exothermic peaks of the (DSC) curve under non-isothermal conditions.

In the present work, the effect of replacement of Te by Sn atoms, on the glass transition and the crystallization kinetics of $Ge_{12}As_{23}Te_{65-x}Sn_x$ (x = 0, 2 and 4 at. %) glassy alloys were studied using DSC results obtained with continuous heating of the sample at different heating rates (non-isothermal conditions). The compositional dependence of the characteristic temperatures (T_g, T_c, T_p), the activation energy of glass transition (E_g) and the activation energy for crystallization (E_c), were discussed. Finally, the crystalline phases that appeared as a result to the crystallization process were identified by using X-ray diffraction (XRD) measurements.

2 Experimental details

Chalcogenide glasses of the composition $Ge_{12}As_{23}Te_{65-x}Sn_x$ (where x = 2, 4 and 6 at. %) system were prepared from Ge, As, Te, and Sn elements with high purity (99.999 %) by the usual melt quench technique. The materials were weighed according to their weights atomic, charged into cleaned silica ampoules and then sealed under vacuum of $\approx 1.33\times 10^{-3}$ Pa. The ampoules were heated into a furnace at around 1350 K for 24 h. During the heating process the ampoules were check several times to maintain their homogeneity, and then the ampoules were quenched in ice cooled water to avoid crystallization. The elemental compositions of these glasses were checked by using energy dispersive x-ray analysis and the estimated average precision was about 0.5% in atomic fraction of each element. The amorphous state of the materials was checked using x-ray diffractometer (Philips type 1710 with Cu as a target and Ni as a filter, λ = 1.5418 A°). The absence of any crystalline peaks confirms the glassy state of the prepared samples.

---

[*] Corresponding author e-mail: Kamalaly2001@gmail.com

The thermal behavior was investigated using calibrated Shimadzu 50 differential scanning calorimeter (DSC). About 15 mg of each sample in powdered form was sealed in standard aluminum pan and scanned over a temperature range from room temperature to about 600 K at different heating rates (β = 2.5, 5, 10, 15, 20 and 30 K/min.).

Density measurements of the considered samples were made by applying Archimedes method using the hydrostatic weighting in toluene. A single crystal of germanium was used as a reference material for determining the toluene density, ρ_{tol}. The samples density (ρ_s) were determined from the relation

$$\rho_s = \frac{W_{air}}{W_{air} - W_{tol}} \rho_{tol}$$

Where W is the weight of the sample. For each composition, the experiment was repeated five times to get the average density of the sample (ρ_s).

3 Results and discussion

Fig.1 shows the x-ray diffraction patterns for the as prepared $Ge_{12}As_{23}Te_{65-x}Sn_x$ chalcogenide glasses. The absence of the diffraction lines in the x-ray patterns confirms the amorphous structures.

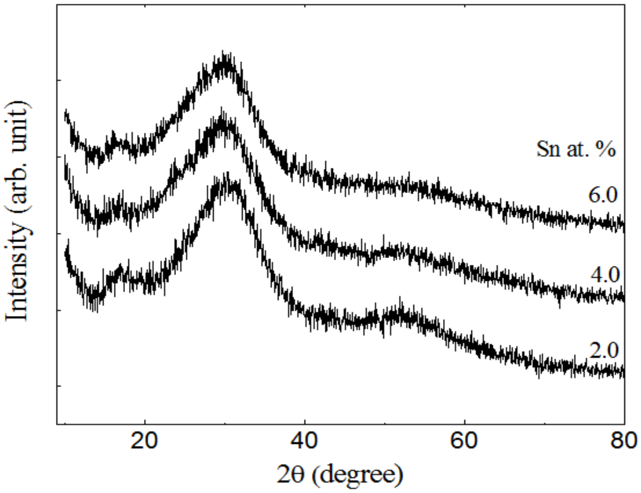

Fig.1 X-ray diffraction patterns of $Ge_{15}As_{20}Te_{65-x}Sn_x$ chalcogenide glasses.

Fig.2 exhibits the DSC traces of the powdered $Ge_{12}As_{23}Te_{63}Sn_4$ chalcogenide glass at different heating rates (β = 2.5, 5, 10, 15, 20 and 30 K/min). This figure shows that there is a very small single endothermic peak. This peak is attributed to the glass transition temperature (T_g) which represents the strength or the rigidity of the glass structure. Also there is an exothermic peak originated from the amorphous-crystalline transformation. The exo peak has two characteristic points: the first point is the onset temperature of crystallization (T_c) and the second is the peak temperature of crystallization (T_p). Fig.3 shows the DSC thermograms of the amorphous $Ge_{12}As_{23}Te_{65-x}Sn_x$ (x = 2, 4 and 6 at. %.) chalcogenide glasses recorded at heating rate 10 K/min. It can be seen from this figure that, the characteristic temperatures (T_g, T_c and T_p) increase with the increase of Sn content. The physical parameters of the elemental compositions are listed in Table 1[17, 18].

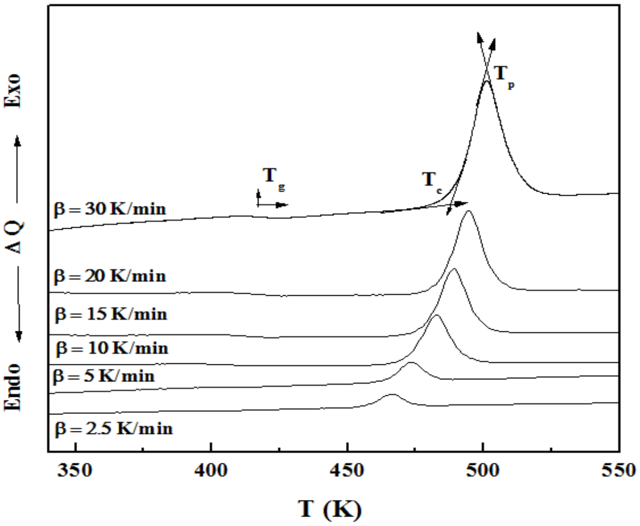

Fig.2 DSC thermograms of $Ge_{15}As_{20}Te_{65}$ chalcogenide glass at different heating rates (β = 2.5, 5, 10, 15, 20 and 30 K/min.

Table 1. The physical parameters of the constituent elements.

Property	Ge	As	Te	Sn
Coordination number [9, 41]	4	3	2	4
H_s (kcal/g tom) [33]	90	69.0	46.0	72
Electronegativity [9, 41]	1.8	2.18	2.1	1.88
Bond energy (KJ mol^{-1}) [9, 41]	65.48	32.10	33	46.7

3.1 Glass transition

Two approaches are used to analyze the dependence of glass transition temperature on the heating rate (β). The first is the empirical relationship:

$$T_g = A + B \ln \beta \qquad (2)$$

where A and B are constants for any given glass composition [19]. The results shown in Fig. 4 indicate the validity of Eq.2 for $Ge_{12}As_{23}Te_{65-x}Sn_x$ (x = 2, 4 and 6 at. %.) glassy alloy and the empirical relationship for this glass can be written in the form of Eq.2 where the A and B values are listed in Table 2.

The second approach concerns with the use of the Kissinger expression [20] for the evaluation of the activation energy for glass transition, (E_g). It has been suggested [21] that, the dependence of the glass transition temperature on β may be written as

$$\ln(T_g^2 / \beta) = -E_g / RT_g + Const. \qquad (3)$$

A straight line between $\ln(T_g^2/\beta)$ and 1/T_g, whose slope yields a value of E_g/R where the subscript g denotes the magnitude values corresponding to the glass transition temperature and R is the gas constant. An expression that originally deduced for the crystallization kinetics, has often been used [21] to calculate E_g.

Table 2. The calculated and measured density and the thermal analysis for $Ge_{15}As_{20}Te_{65-x}Sn_x$ (x = 0, 2 and 4 at. %) chalcogenide glasses.

Sn at. %	A	B	Tg (K)	T_c (K)	Tp (K)	Eg [32]	Eg [34]	<Eg >	Ec[17] kcal/mol	K_o (s^{-1})	N_r^*	Te-Te	N_c^*	Hs* kcal/g.atom	CE	D g/cm^{-3}
						kcal/mol										
2	420	10.1	399	469	482	27.58	29.57	28.58	30.4	5.53×10^{11}	2.50	59	3.18	28.29	43.998	5.9
4	433	10.6	410	470	485	32.22	32.59	32.4	34.23	7.33×10^{12}	2.58	53	3.23	28.41	45.182	5.97
6	440	9.85	422	475	487	37.43	37.9	37.66	39.15	2.24×10^{15}	2.64	47	3.28	28.53	46.365	6.15

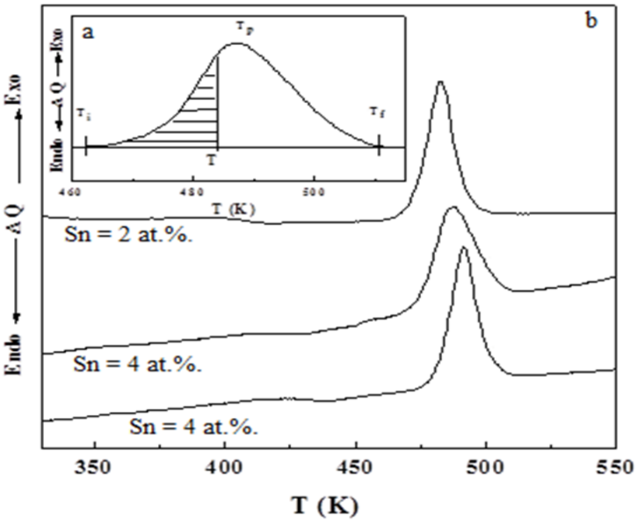

Fig.3. DSC thermograms of $Ge_{15}As_{20}Te_{65-x}Sn_x$ chalcogenide glasses recorded at heating rate 10 K/min.

In addition, if it is assumed that, usually, the change in $\ln(T_g^2)$ with β is negligibly small compared with the change in ln β [22], one obtains

$$\ln(\beta) = -E_g/RT_g + Const. \qquad (4)$$

A straight line, whose slope also yields a value of E_g/R.

Fig. 5 Shows plots of $\ln(\beta/T_g^2)$ and ln(β) versus 1/T_g for the $Ge_{12}As_{23}Te_{65-x}Sn_x$ semiconductor glass, displaying the linearity of the two equations used. The obtained values of the glass transition activation energies <E_g> were found to increases with increasing Sn content (see Table.2).

The deduced values of E_g lie within the observed values for chalcogenide glasses [9, 23-25]. The observed increase in E_g values with increasing Sn content resulted in an apparent increase of the T_g values. These results are in good agreement with those obtained by Cofmenero et al.[21]. Therefore, the glasses rigidity increases with increasing Sn content. The glass transition temperature is known to depend on several independent parameters such as the band gap, bond energy, effective molecular weight, the type and fraction of various structural units formed and the average coordination number [26]. Ioffe et al [27] suggested that the bonding character in the nearest-neighbor region, which means the coordination number (N_r), characterizes the electronic properties of semiconducting materials. The average coordination number (N_r)in the studied samples can be calculated by the equation [28]

$$N_r = 4XGe + 3XAs + 2XTe + 4XSn$$

Where X is the mole fraction. The determination of N_r allows the estimation of the number of constraints (N_s).

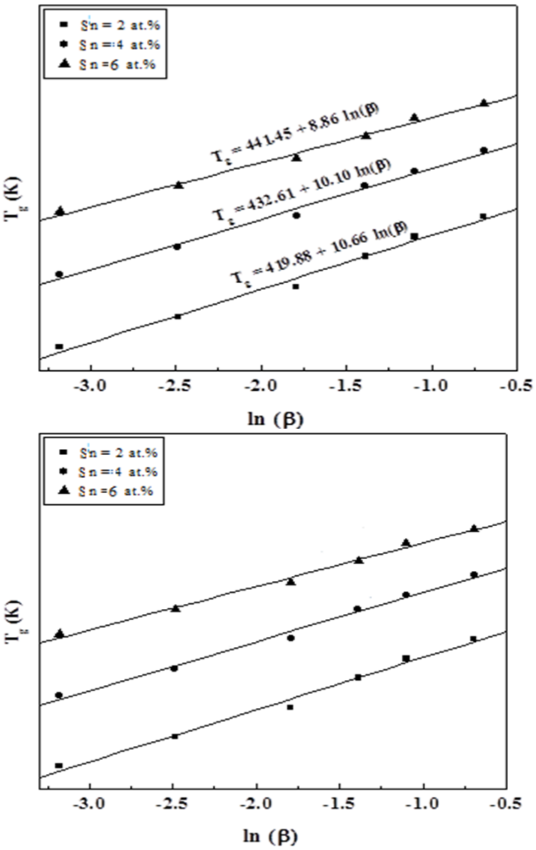

Fig.4. T_g vs. ln (β) $Ge_{15}As_{20}Te_{65-x}Sn_x$ (x = 2, 4 and 6 at.%) chalcogenide glasses.

This parameter is closely related to the glass-transition temperature and its related properties. For a material with coordination number (N_r),N_s can be expressed as the sum of the radial and angular valence force constraints [29],

$$N_s = \frac{N_r}{2} + 2\,(N_r\ -3)$$

The calculated data of N_r and N_s of the $Ge_{12}As_{23}Te_{65-x}Sn_x$ system are listed in Table 2, using the values of N_r for Ge, As, Te and Sn [9, 30, 31] given in Table 1. It can be seen that both N_r as well as N_s decreases with increasing Te content.

According to Pauling [32], the heat of atomization $H_S(A-B)$, at standard temperature and pressure of a binary semiconductor formed from atoms A and B is the sum of the heat of formation ΔH and the average of the heats of atomization $H_S{}^A$ and $H_S{}^B$ that corresponds to the average non-polar bond energy of the two atoms, and it can be calculated from the following eqution:

$$H_s\,(A-B) = \Delta H + \frac{1}{2}\,(H_s{}^A + H_s{}^B)$$

The first term in eq.(7) is proportional to the square of the difference between the electronegativities χ_A and χ_B of the two atoms

$$\Delta H\ \alpha\ (\chi_A - \chi_B)^2$$

This idea was extended to quaternary semiconductors compounds by Sadagopan and Gotos [33].

In most cases, the heat of formation of chalcogenide glasses is unknown. In the few materials for which it is known, its value does not exceed 10% of the heat of atomization and therefore can be neglected [30, 34][5, 36]. Hence, $H_S(A-B)$ is given quite well by

$$H_S\,(A-B) = \frac{1}{2}\,(H_S{}^A + H_S{}^B)$$

The obtained results of the average heat of atomization of $Ge_{15}As_{20}Te_{65-x}Sn_x$ (where x = 0, 2 & 4 at. %) glasses are listed in Table 2, using the values of H_S for Ge, As, Te and In given in Table 1. The bond energies $D(A-B)$ for heteronuclear bonds have been calculated by using the following empirical relation

$$D(A-B) = [\,D(A-A).D(B-B)]^2 + 30\,(\chi_A - \chi_B)^2$$

proposed by Pauling [35], where $D(A-A)$ and $D(B-B)$ are the energies of the homonuclear bonds (in units of kcal/mol.) [18, 30, 36], χ_A and χ_B are the electronegativity values for the involved atoms [30, 37]. Bonds are formed in the sequence of decreasing bond energy until the available valence of atoms is satisfied [38].In the present compositions, the Ge-Sn bonds with the highest possible energy (42.411 kcal. mol^{-1}) are expected to occur first, since the Ge-Te bonds (35.468 kcal mol^{-1}) followed by As-Te bonds (32.73 kcal mol^{-1}) to saturate all available valence of Te. There are As-Sn and Te-Sn bonds with high formation probability but, The Sn amount is not sufficient to saturate both As and Te valences.

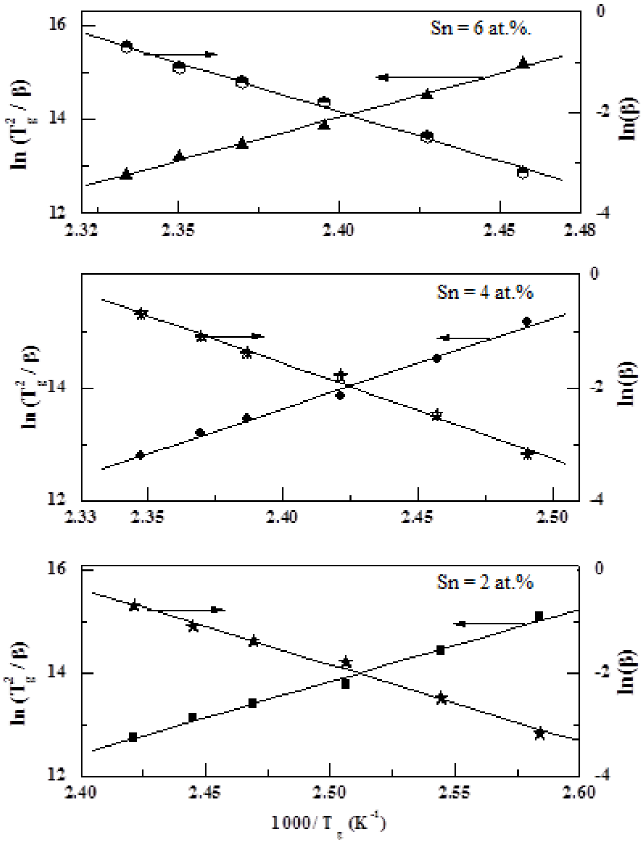

Fig.5. $\ln(T_g^2/\beta)$ vs. 1/Tg, (b) ln(β) vs $1/T_g$ for different compositions of $Ge_{15}As_{20}Te_{65-x}Sn_x$ (x = 2, 4 and 6 at.%) chalcogenide glasses.

(9)

After the formation of Ge-Sn, Ge-Te and As-Te bonds are formed; there is still unsatisfied Te valence, which must be satisfied by the formation of Te-Te. As it was explained, the glass transition behavior of the amorphous systems in terms of cohesive energy (CE) reflects the average bonds strength, and in the same time, allows the determination of bonds between like atoms if there is an excess of certain type of atoms, until all available valences for the atoms are saturated. Based on the chemical bond approach, the bond energies are assumed to be additive. Thus, the cohesive energies (CE) were estimated by summing the bond energies over all the bonds expected in the material. Calculated values of the cohesive energies for all compositions are presented in Table 2. These results indicate that, the cohesive energies of these glasses increase with increasing Sn content. It should be mentioned that, the approach of the chemical bond neglects dangling bond and other valence defects as a first approximation. Also van der

Walls interactions are neglected, which can provide means for further stabilization by the formation of much weaker links than regular covalent bonds.

3.2 Crystallization kinetics

For the evaluation of the activation energy for crystallization (E_c) and the frequency factor (K_0) from the variation of T_p with β [38], the following equation can be used

$$\ln(T_p^2/\beta) = -E_c/RT_p - \ln(K_0R/E) \qquad (11)$$

The plot of $\ln[T_p^2/\beta]$ vs. $1/T_p$ is shown in Fig.6. The deduced values of E_c and K_o were listed in Table (2).

The area under the DSC curve is directly proportional to the total amount of the alloy crystallized. The ratio between the ordinates and the total area of the peak gives the corresponding crystallization rates which make it possible to plot the curves of the exothermal peaks represented in Fig(7). It is observed that, the $(dx/dt)_p$ values increases with the increase of the heating rate, a property which has been widely discussed in the literature [10, 39, 40].

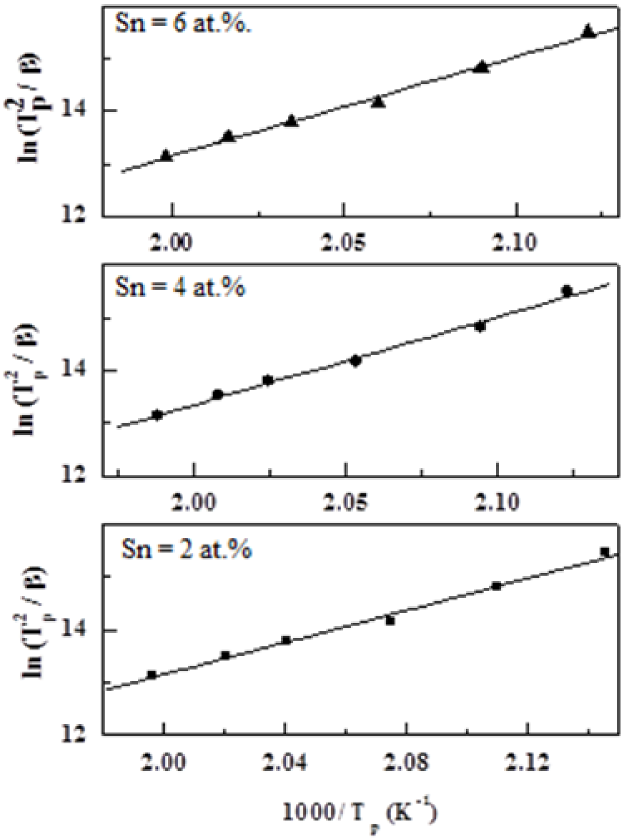

Fig.6 $\ln(T_g^2/\beta)$ vs. 1/Tg, for different compositions of $Ge_{15}As_{20}Te_{65-x}Sn_x$ (x = 2, 4 and 6 at. %) chalcogenide glasses.

With the aim of the correct applying of the preceding theory, the materials were reheated up to a temperature slightly higher than T_g for 1 hr in order to form a large number of nuclei. It was ascertained by X-ray diffraction that, there are small crystalline peaks were detected after the nucleation treatment for Sn = 0 and Sn =2 at.% while there is no crystalline peaks were detected after the nucleation treatment for Sn content = 4 at.% Furthermore both the numerical factors n and m (that dependence on the crystallization mechanism and the dimensional of the crystal growth) can be calculated by using the obtained values of the crystallization rate $(dx/dt)_p$ [10] (see Fig.7) through the following two equations

$$\dot{\chi}_p = n(0.37\beta E_c)/(RT_p^2) \qquad (12)$$

$$\dot{\chi}_p = mE\beta(1-\chi_p)/RT_p^2\ ) \qquad (13)$$

From the experimental data it has been observed that the correlation coefficients of the corresponding straight regression lines show a maximum value for a given temperature, which was considered as the most adequate one for the calculation of the parameters n,and m by using Eqs.12, 13 respectively. It was found that with respect to the three samples the <n> values for the as-quenched glasses are 3.0, 2.0 and 2.0 respectively, while the <m> values for the reheated glasses are 2.0, 1.0 and 2.0 respectively. Both values for Sn = 0 and Sn = 2 at.% the n values for the as-prepared glassed and the reheated have different values, this indicates that the as prepared glasses containing no nuclei, therefore n = m +1 for the two samples with (Sn = 0 at.% and 2 at.% respectively).

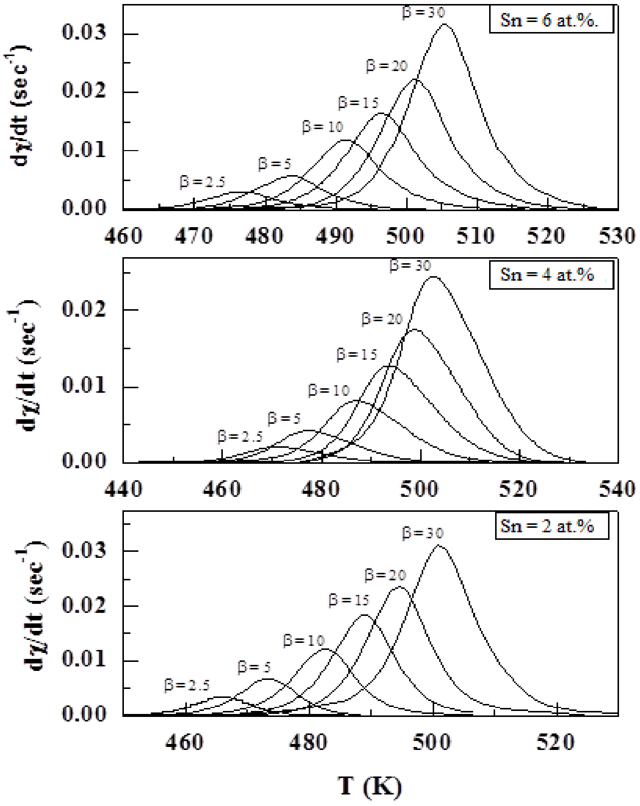

Fig.7 Crystallization rate (dχ/dt) versus temperature of the exothermal peaks at different heating rates of

$Ge_{15}As_{20}Te_{65-x}Sn_x$ (x = 2, 4 and 6 at. %) chalcogenide glasses.

The n values of the as-prepared and the reheated glass with Sn content = 4 at.%, allowing the experimental error, both values are close to each other which indicates that, a large number of nuclei exist already in the material, and therefore $m = n = 2$ for $Ge_{15}As_{20}Te_{61}Sn_4$ glass. From the mean value of the kinetic exponent, (n), it is possible to postulate a crystallization reaction mechanism. Mahadevan et al. [23] have shown that n may be 4, 3, 2, or 1, which are related to different crystallization mechanisms: $n = 4$, volume nucleation, three-dimensional growth; $n = 3$, volume nucleation, two-dimensional growth; $n = 2$, volume nucleation, one-dimensional growth; $n = 1$, surface nucleation, one-dimensional growth from surface to the inside.

The deduced E_c values for $Ge_{15}As_{20}Te_{65-x}Sn_x$ glasses were listed in Table2. From this table it can be notice that the activation energy of crystallization increases with increasing Sn content as a result of increasing T_p values. Finally, The addition of Sn at the expense of Te in $Ge_{15}As_{20}Te_{65-x}Sn_x$ glasses results in a monotonic increase in the density while the molar volume (V_m) decrease as shown also in Table 2. It is well known that, the density and molar volume changes are related to the change in the atomic weight and the atomic volume of the elements constituting the system.

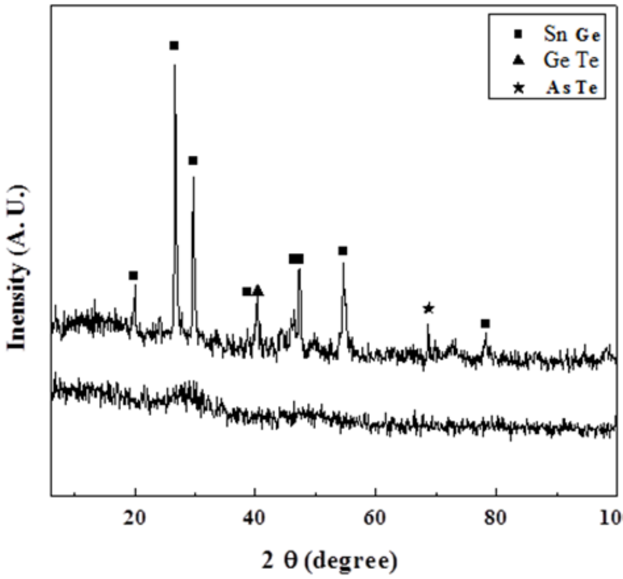

Fig.8 Diffractogram of $Ge_{15}As_{20}Te_{65-x}Sn_x$ glassy alloy (a) as prepared (b) after thermal treatment (annealing at T_p for 2 H).

4 Conclusions

The described theoretical method enables us to study the evolution of nuclei with the time of the volume fraction crystallized in materials involving crystal growth processes. This procedure assumes the concept of the extended volume of transformed material and the condition of randomly located nuclei. Using these assumptions we have obtained a general two expressions for the volume fraction crystallized, as a function of the temperature in bulk crystallization processes that enables us to determine the numerical factors n and m. The addition of Sn at the expense of Te in $Ge_{15}As_{20}Te_{65-x}Sn_x$ glasses result in an apparent increase the characteristic temperatures (T_g, T_c, T_p) as well as the activation energy of both glass transition and glass crystallization. The observed results were successfully related to the average coordination number, the average heat of atomization and the cohesive energy.

References

[1] J.C. Phillips, The Fundamental Optical Spectra of Solids, in: Solid State Physics - Advances in Research and Applications, 1966, pp. 55-164.

[2] S.R. Ovshinsky, D. Adler, Progress in the science and application of amorphous materials, Journal of Non-Crystalline Solids, 90 (1987) 229-241.

[3] M. Itoh, K. Tanaka, M. Kitao, Localized-state distributions in Ag-modified As2Se3 glasses, Japanese Journal of Applied Physics, Part 2: Letters, 34 (1995) L487-L490.

[4] M.M. El-Ocker, M.H. El-Fouly, S.A. Fayek, H. Talaat, G.A.M. Amin, Effect of In addition on some physical properties of the As2Se3 amorphous system, Applied Physics A: Materials Science & Processing, 60 (1995) 233-238.

[5] P. Sharma, S.C. Katyal, Effect of Ge addition on the optical band gap and refractive index of thermally evaporated As2Se3 thin films, Advances in Materials Science and Engineering, 2008 (2008).

[6] A.A. Othman, K.A. Aly, A.M. Abousehly, Effect of Te additions on the optical properties of (As-Sb-Se) thin films, Thin Solid Films, 515 (2007) 3507-3512.

[7] K.A. Aly, A.M. Abousehly, A.A. Othman, Photoelectrical properties of (Sb15As30Se55)100-xTex (0 ≤ x ≤ 12.5 at.%) thin films, Journal of Non-Crystalline Solids, 354 (2008) 909-915.

[8] A.A. Othman, K.A. Aly, A.M. Abousehly, Glass transition and crystallization kinetics of Sb 14.5As 29.5Se 53.5Te 2.5 amorphous solid, Physica Status Solidi (A) Applications and Materials Science, 203 (2006) 837-843.

[9] K.A. Aly, A. Dahshan, F.M. Abdel-Rahim, Thermal stability of Ge-As-Te-In glasses, Journal of Alloys and Compounds, 470 (2009) 574-579.

[10] K.A. Aly, M.Y. Hassaan, Y.B. Saddeek, Thermal features and physical properties of sulfur modified barium vanadate glasses, Phase Transitions, 86 (2013) 477-489.

[11] K.A. Aly, Y.B. Saddeek, A. Dahshan, Structure and crystallization kinetics of manganese lead tellurite glasses, Journal of Thermal Analysis and Calorimetry, (2014).

[12] N. Mehta, M. Zulfequar, A. Kumar, Kinetic parameters of crystallization in glassy Se 100-xSb x alloys, Physica Status

Solidi (A) Applications and Materials Science, 203 (2006) 236-246.

[13] G. Zhang, D. Gu, X. Jiang, Q. Chen, F. Gan, Crystallization of amorphous Ge2Sb2Te5 films induced by a single femtosecond laser pulse, Solid State Communications, 133 (2005) 209-212.

[14] M. Abu El-Oyoun, A study of the crystallization kinetics of Ge2QTe80 chalcogenide glass, Journal of Physics D: Applied Physics, 33 (2000) 2211-2217.

[15] J. Vázquez, C. Wagner, P. Villares, R. Jimenez-Garay, A study of the glass forming ability of some alloys in the Ge-As-Te system by differential scanning calorimetry, Materials Chemistry and Physics, 58 (1999) 187-190.

[16] N.B. Maharjan, D. Bhandari, N.S. Saxena, D.D. Paudyal, M. Husain, Kinetic studies of bulk Se85-xTe15Sbx glasses with x = 0, 2, 4, 6, 8 and 10, Physica Status Solidi (A) Applied Research, 178 (2000) 663-670.

[17] S.A. Fayek, S.S. Fouad, M.R. Balboul, M.S. El-Bana, Crystallization kinetics in As-Se-Sn glassy system, Physica B: Condensed Matter, 388 (2007) 230-236.

[18] L. Tichý, A. Tříska, H. Tichà, M. Frumar, J. Klikorka, The composition dependence of the gap in amorphous films of SixGe1-x, SbxSe1-x and AsxTe1-x systems, Solid State Communications, 41 (1982) 751-754.

[19] M. Lasocka, The effect of scanning rate on glass transition temperature of splat-cooled Te85Ge15, Materials Science and Engineering, 23 (1976) 173-177.

[20] H.E. Kissinger, Reaction kinetics in differential thermal analysis, Analytical Chemistry, 29 (1957) 1702-1706.

[21] J. Colmenero, J.M. Barandiaràn, Crystallization of Al23Te77 glasses, Journal of Non-Crystalline Solids, 30 (1979) 263-271.

[22] J. Sestak, APPLICABILITY OF DTA TO THE STUDY OF CRYSTALLISATION KINETICS OF GLASSES, Physics and Chemistry of Glasses, 15 (1974) 137-140.

[23] S. Mahadevan, A. Giridhar, A.K. Singh, Calorimetric measurements on as-sb-se glasses, Journal of Non-Crystalline Solids, 88 (1986) 11-34.

[24] M. Zulfeqaur, Z.H. Khan, M. Husain, P.J. Sebastian, Thermal studies of a-Ga20Se80-xTex semiconducting alloys, in, SPIE, Delhi, India, 1998, pp. 1291-1294.

[25] L. Zauski, A. Zauska, M. Lasocka, Thermal evidence of structural phase transformation in Te-Ge-Sb and Te-Ge-Bi systems, Journal of Materials Science, 15 (1980) 1331-1333.

[26] A. Giridhar, S. Mahadevan, The Tg versus Z dependence of glasses of the GeInSe system, Journal of Non-Crystalline Solids, 151 (1992) 245-252.

[27] A. Dahshan, K.A. Aly, Characterization of new quaternary Ge20Se60Sb20 - XAgx (0 ≤ x ≤ 20 at.%) glasses, Journal of Non-Crystalline Solids, 408 (2015) 62-65.

[28] P. Sharma, A. Dahshan, K.A. Aly, New quaternary Ge-Se-Sb-Ag optical materials: Blue shift in absorption edge and evaluation of optical parameters, Journal of Alloys and Compounds, 616 (2014) 323-327.

[29] J.C. Phillips, M.F. Thorpe, Constraint theory, vector percolation and glass formation, Solid State Communications, 53 (1985) 699-702.

[30] S.A. Fayek, S.S. Fouad, Topological consideration of thallium on glassy arsenous selenide, Vacuum, 52 (1999) 359-363.

[31] K.A. Aly, F.M. Abdel-Rahim, Effect of Sn addition on the optical constants of Ge-Sb-S thin films based only on their measured reflectance spectra, Journal of Alloys and Compounds, 561 (2013) 284-290.

[32] L. Pauling, The dependence of bond energy on bond length, Journal of Physical Chemistry, 58 (1954) 662-666.

[33] V. SADAGOPAN, H.C. GATOS, on the relationship of semiconductor compound properties and the average heats of atomisation, Solid-State Electronics, 8 (1965) 529-534.

[34] S.S. Fouad, A.H. Ammar, M. Abo-Ghazala, The relationship between optical gap and chemical composition in SbxSe1-xsystem, Vacuum, 48 (1997) 181-184.

[35] L. Pauling, The nature of the chemical bond. II. The one-electron bond and the three-electron bond, Journal of the American Chemical Society, 53 (1931) 3225-3237.

[36] L. Tichý, H. Tichá, M. Frumar, J. Klikorka, A. Tříska, C. Barta, A. Němečková, Index of refraction and d. c. electrical conductivity in Ge40-xSbxS60 glasses, Czechoslovak Journal of Physics, 32 (1982) 1363-1373.

[37] J. Bicerano, S.R. Ovshinsky, Chemical bond approach to glass structure, Journal of Non-Crystalline Solids, 75 (1985) 169-175.

[38] K.A. Aly, F.M. Abdel Rahim, A. Dahshan, Thermal analysis and physical properties of Bi-Se-Te chalcogenide glasses, Journal of Alloys and Compounds, 593 (2014) 283-289.

[39] B.S. Patial, N. Thakur, S.K. Tripathi, Crystallization study of Sn additive Se-Te chalcogenide alloys, Journal of Thermal Analysis and Calorimetry, 106 (2011) 845-852.

[40] I. Avramov, J. Šesták, Generalized kinetics of overall phase transition explicit to crystallization, Journal of Thermal Analysis and Calorimetry, (2014).

[41] M.A. Abdel-Rahim, A. Gaber, A.A. Abu-Sehly, N.M. Abdelazim, Crystallization study of Sn additive Se-Te chalcogenide alloys, Thermochimica Acta, 566 (2013) 274-280.