

A new concept of glass transition and modification of Johnson-Mehl-Avrami equation in chalcogenide glass Ge-Sb-Te

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In this paper, a new concept of glass-crystal transition is proposed. It was found that the cooling rate has strong influence on the composition and crystallization process of chalcogenide glasses based in the system Ge-Sb-Te. We have modified the equation Johnson-Mehl-Avrami in order to evidence the crystallization fraction at peak maxima. The non-isothermal transition of Ge-Sb-Te has been investigated using different methods: Kissinger, Takhor, Augis and Bennett, Matusita and Sakka.

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1. Introduction

The crystallization of GeSbTe glasses alloys has been the subject of numerous studies [1-5], because of the potential technological applications in memory devices [6-7]. The study of the crystallization processes of chalcogenide glasses is of considerable interest and affords important information about the changes of the physical and thermal properties during glass-crystal transition [8-12].

The understanding of glass crystal transition is a challenging problem. The glass-crystal transition directly depends on the methods of fabrication of glass. The glass transition occurs in the process of cooling of the chalcogenide liquids. All the methods proposed for the study of crystallization kinetics are based on thermo-analytical techniques, such as differential thermal analysis, DTA, or differential scanning calorimetry DSC. In general, several methods were developed from the famous equation Johnson-Mehl-Avrami [13-14] to determine the activation energy of crystallization, which were reported by H. Yinnon and D. R. Uhlmann [15]. In the present study of crystallization kinetics of Ge-Sb-T in non-isothermal regime is discussed the role-played by cooling rate on composition and crystallization parameters.

2. Experimental

The preparation of the samples consists in two steps. First, the three elements (99.999% purity) in suitable quantities are introduced into a quartz ampoule and sealed in a vacuum of 10^{-5} Pa. Then the ampoule was heated above 1000 °C and quenched in air. The composition of the bulk alloys was checked by atomic absorption spectrometer (Perkin Elmers 2380). The ingots were

ground down to affine powder and placed in a capillary tube sealed under vacuum. The samples were annealed up to 1000 °C and quenched in water. The amorphicity of the sample is checked by X-ray diffraction, The thermograms were recorded using a Setaram DSC92 at different heating rates (7, 10, 15 °C/min).

3. Theoretical basis

The interpreting of the DSC results under non-isothermal condition

$$T = \alpha t + T_0 \quad (1)$$

where T_0 is the initial temperature general is 25 °C and α is the heating rate, is based on the equation(2) which describes the evolution of the crystallized fraction x with time t [13-14].

$$x = 1 - \exp - Kt^n \quad (2)$$

Here n is an integer which depends on the mechanism of growth and the dimensionality of the crystal and K is the jump frequency.

K is generally assigned for an Arrhenian temperature dependence (3).

$$K = K_0 \exp \frac{-E}{RT} \quad (3)$$

where E represents the activation energy, T is the temperature and R is the gas constant. By differentiating equation (2) results the following expression:

$$\dot{x} = (1-x)nK t^{n-1} \left(1 + \frac{t}{K} \dot{K}\right) \tag{4}$$

where $\dot{x} = \frac{dx}{dt}$ and $\dot{K} = \frac{dK}{dt}$, the derivatives of K with respect to time are obtained from eqs (3)

$$\dot{K} = \frac{dK}{dT} \frac{dT}{dt} = \alpha \frac{d}{dT} \left[K_0 \exp\left(-\frac{E}{RT}\right) \right] \tag{5}$$

$$\dot{K} = \frac{\alpha EK_0}{RT^2} \exp\left(-\frac{E}{RT}\right) \tag{6}$$

Thus eq (4) becomes

$$\dot{x} = (1-x)nK t^{n-1} (1+at) \tag{7}$$

where $a = \frac{\alpha E}{RT^2}$. If T_0 in eq. (1) is much smaller than T, the term $at \approx \frac{E}{RT}$. For the cases where $\frac{E}{RT} \ll 1$ eq. (4) becomes

$$\dot{x} = (1-x)nK t^{n-1} \tag{8}$$

3.1 Method of Takhor

Takhor [16], developed a method based on eq. (8), which suggested that the maximum rate of crystallization occurs at the exothermic peak, at time t^P to temperature T^P and assuming that K is independent on time in the differentiation of eq. (8).

$$\dot{x} = nK t^{n-2} \left[(n-1) - nK t^n \right] = 0 \tag{9}$$

By changing time t^P to temperature T^P using eqs (1), and (9) one gets

$$n \ln \alpha - n \ln(T^P - T_0) = \ln \frac{nK_0}{n-1} - \frac{nE}{RT^P} \tag{10}$$

The value of x^P the fraction crystallized at the maximum of the exothermic peak, it is readily seen from equation (9) that

$$(Kt)^n = \frac{n-1}{n} \tag{11}$$

By substituting eq (11) in eq (2) one obtains

$$x^P = 1 - \exp\left(-\frac{n-1}{n}\right) \tag{12}$$

3.2 Method of Augis and Bennett

Using a similar principle as in the Takhor method, Augis and Bennett [17], substituted u for Kt and wrote eq. (8) as

$$\dot{x} = nu^{n-1}(1-x) \tag{13}$$

where $\dot{x} = \frac{du}{dt}$. The differentiation eqs (13) leads to

$$\dot{x} \left[nu - \dot{x}^2 (nu^n - n + 1) \right] nu^{n-2} (1-x) = 0 \tag{14}$$

where $\dot{x} = \frac{d^2u}{dt^2}$. If $u = Kt$ it can be shown that

$$\dot{x} = u \left(\frac{1}{t} + a \right) \tag{15}$$

$$\dot{x} \approx u \left[\left(\frac{1}{t} + a \right)^2 - \frac{1}{t^2} \right] - 2 \frac{au}{t} \tag{16}$$

which results to

$$\dot{x} = a^2 u \tag{17}$$

The combination between eq (15), eq (17) and eq (14), the following expression is obtained

$$nu^n - n + 1 = \left(\frac{at}{1+at} \right)^2 \tag{18}$$

For $at \ll 1$ eq (18) $nu^n - n + 1 = 0$ becomes (19) similar to eq. (9) of Takhor.

For $at \gg 1$ eq. (18) becomes

$$u = Kt = K_0 \exp \frac{E}{RT^P} \frac{T^P - T_0}{\alpha} = 1 \tag{20}$$

in logarithmic form

$$\ln K_0 - \frac{E}{RT^P} + \ln \left(\frac{T^P - T_0}{\alpha} \right) = 0 \tag{21}$$

The value of x^P at T^P when replacing eq. (20) in eq. (2) is:

$$x^P = 0.63 \tag{22}$$

3.3 Method of Kissinger

The majority of studies used Kissinger method [18], is based on eq. (2). By substituting t from eq. (2) and replacing in eq. (8)

$$\dot{x} = (1-x)nK \left[-\ln(1-x) \right]^{\frac{(n-1)}{n}} \tag{23}$$

Kissinger has considered that the function $\left[-\ln(1-x) \right]^{\frac{(n-1)}{n}}$ is constant with x and using similar approach of Takhor's method the maximum of the crystallization rate at the exothermic peak eqs (23) becomes

$$\dot{x} = \left| \frac{E}{RT^{P+2}} - \frac{AK_0}{\alpha} \exp^{-E/RT^P} \right| \alpha K_0 (1-x^P) \exp^{-E/RT^P} = 0 \tag{24}$$

or in logarithmic form

$$\ln \frac{\alpha}{1-P^2} = -\frac{E}{RT^P} + \ln \frac{AR K_0}{E} \quad (25)$$

3. 4 Theory of Matusita and Sakka

Matusita [19] proposed, method for the analyses non-isothermal crystallization kinetics on the basis of nucleation and growth process, using the volume fraction of crystal, x, expressed by

$$\frac{dx}{dt} = 4\pi N r^2 (1-x) \frac{dr}{dt} \quad (26)$$

In this equation N represents the number of nuclei per unit volume, $\frac{dr}{dt} = U$ is the rate of crystal growth expressed by the following equation

$$U = U_0 \exp\left(-\frac{E}{RT}\right) \quad (27)$$

which shows that the crystallized fraction(x) can be described as a function of time t according to the following formula:

$$\ln(-\ln(1-x)) = -n \ln \alpha - 1.052 \left(\frac{mE}{RT}\right) + const. \quad (28)$$

where n and m describes the process of crystallization. When the number of nuclei is inversely proportional to the heating rate then m is equal to n-1, If the number of nuclei does not change with the heating rate then m is equal to n .

4. Results and discussion

From the previous thermal study of the peritectic composition $Ge_{15.5-x}Te_{84.5}Sb_x$ (x= 0.5, 1, 1.5) [20,21], we have considered the double glass transition T_{g1} , T_{g2} correspond to the germination of free chains of tellurium in hexagonal form and tellurium chains trapped by GeTe chains, respectively, followed by two peaks of crystallization. It is remarkable that the value of T_{g1} decreases when antimony content increases. However the value of T_{g2} increases. This is illustrated in Fig. 1. The explanation is that antimony eliminated some amount of tellurium from GeTe chains (see Fig. 2). This supports the hypothesis that high Ge amount causes an obstacle against the crystallization process of the tellurium. In the results of Kaban and al [22] evidenced, the same effect of Germanium on the glass temperature in Ge_xTe_{100-x} for x = 10, 15, 20, 25 (Table 1).

Table 1. The values of T_g at the heating rate of $10^\circ C/min$.

Composition	$Ge_{10}Te_{90}$	$Ge_{15}Te_{85}$	$Ge_{20}Te_{80}$	$Ge_{25}Te_{75}$
T_g [22]	105.4	133.2	156.5	180.9
Composition	$Ge_{15}Te_{84.5}Sb_{0.5}$	$Ge_{14.5}Te_{84.5}Sb_1$	$Ge_{14}Te_{84.5}Sb_{1.5}$	$Ge_{13}Te_{84.5}Sb_{2.5}$
T_{g1}	122	117	115	108
T_{g2}	145	147	150	-----

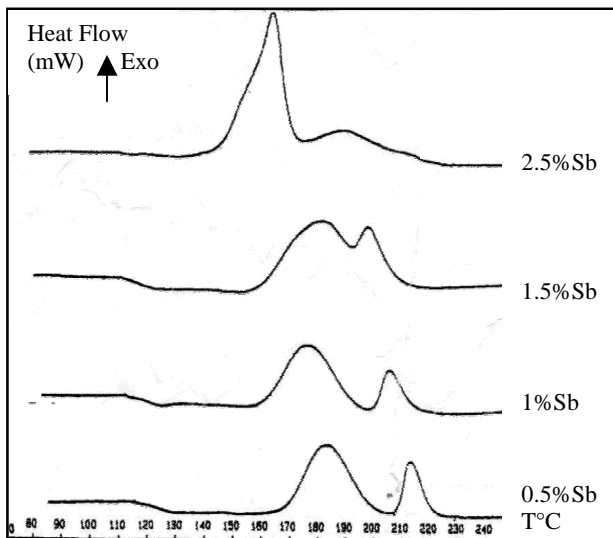


Fig .1.The thermograms of the alloys $Ge_{15.5-x}Te_{84.5}Sb_x$ (x= 0.5, 1, 1.5, 2.5) at the rate of $10^\circ C/min$.

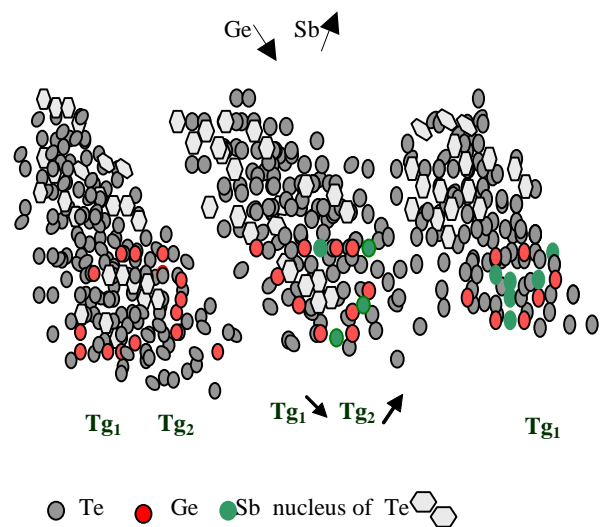


Fig .2. The role of Antimony in the crystallization process of $Ge_{15}Te_{85}$.

It is well known that the glass temperature represents the temperature of the formation of the glassy chalcogenide in the cooling process. According to the definition, the vitreous transition is an endothermic reaction (absorption of energy) in DSC thermograms. Few studies [23] explained this absorption of energy due to the formation of different bonds existing in glass. If this is true, the glass temperature is independent of heating rate in non-isothermal crystallization. However, the increase in heating rate usually accompanies the increase of the value of T_g . According to these concepts and model of glass transition in $Ge_{15}Te_{85}$ [20], we can ask the questions:

-How GeTe causes a difficulty to the formation of the first nucleus of Te-Te chains?

-What kind of obstacle is formed in order to stop the construction of the crystal in cooling at T_g and destroy it by heating at the same temperature T_g ?

The glass chalcogenide is constituted from free atoms, free ions, chains of atoms, chains of atoms and ions, chains of ions, free electrons, free holes, and defects. One of the important constituents are defects but it is not a direct relation between defects and T_g . The defects create traps for electrons. The density of free electrons is higher in liquid glass, that is equivalent to high density of Te^{2+} , Te^{3+} , and Te^{4+} . The formation of tellurium glass is based on the conservation of the density of free electrons existing in liquids in the traps of the Tellurium glass, when the liquid

glass chalcogenide is quenched from the high temperature to low temperature state. Thus, the dominance of Coulomb energy is a result of the recombination of **electron- Te^+** that accompanies the formation of traps for the reason of the rapid arrangement of the chains of tellurium during cooling process and the presence of another type of chains GeTe. We suggest that formation of glass chalcogenide is due to the formation of quasi-particles which are excitons in disordered system $Te^{n+} - e^-$. Further consider that the absorption of energy at T_g destroys the bonds between the Te^{n+} and e^- localized at distance in trap. When we heat the glass at a given heating rate the electron absorbs the thermal energy kT to move from one site of trap to another site of trap by hopping phenomenon [24], in the direction of the attraction force of Te^{n+} . As a consequence, the bond energy $Te^{n+} - e^-$ becomes higher. This can explain the proportionality of T_g values with the heating rate. Identical phenomena produced in glass chalcogenide aged at temperature T in period t as an effect of the existence of important endothermic effect at peak T_g , the existence of small crystallites in aged glass chalcogenide caused by the mechanism of relaxation is a consequence of the recombination of a few pairs $Te^{n+} - e^-$, (to the accessible traps). This releases the tellurium atom. There are two categories of excitons: $Te^{n+} - e^-$, and $Te^{n+} - e^- - Te^{n+}$. Fig. 3 illustrates our ideas.

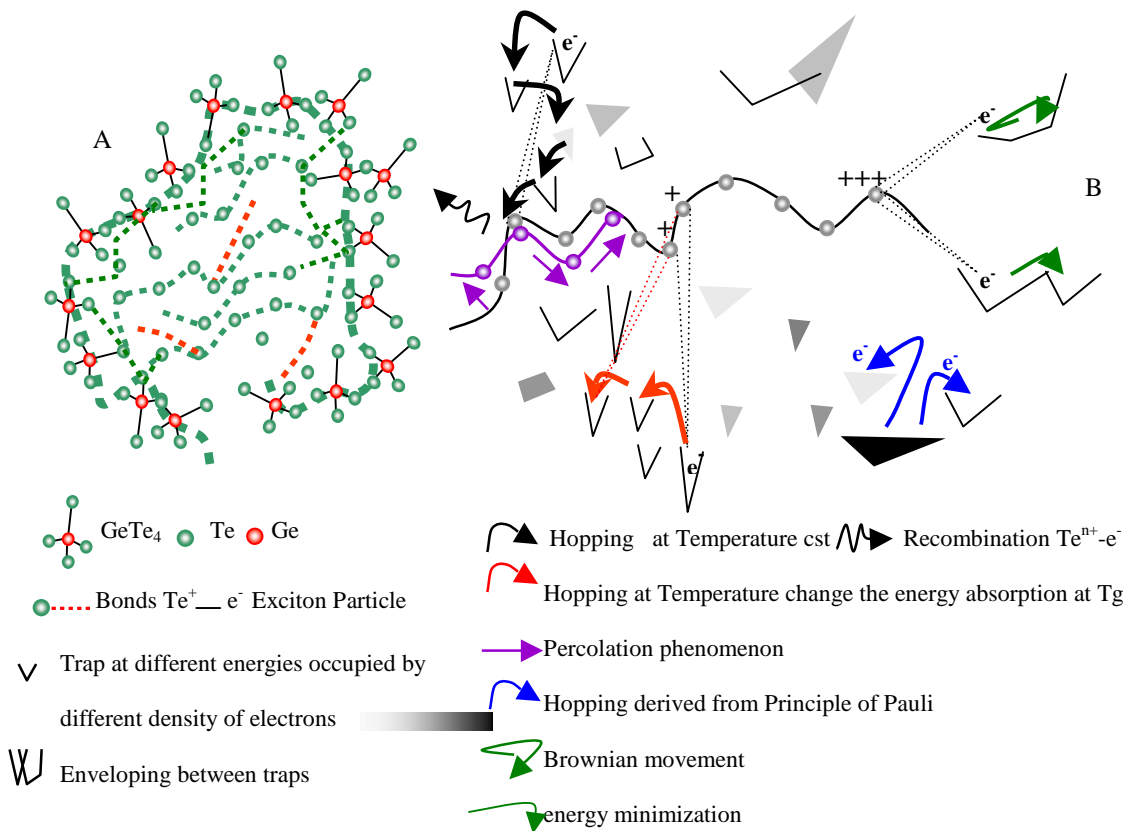


Fig .3. A. The effect of GeTe chains on Tellurium chains. B. The devitrification process in Tellurium chain.

Fig. 4a shows a typical DSC curve recorded on $\text{Ge}_{13.5}\text{Te}_{84.5}\text{Sb}_2$ heated at a constant rate of $10^\circ\text{C}/\text{min}$. Three characteristic are observed. The first T_g corresponds to the glass transition temperature at 140°C followed by an exothermal peak representing the crystallization which starts at 228°C , and last temperature corresponding to the fusion endothermal peak at 396°C . Fig. 4b exhibits the variation of thermograms DSC with heating rate.

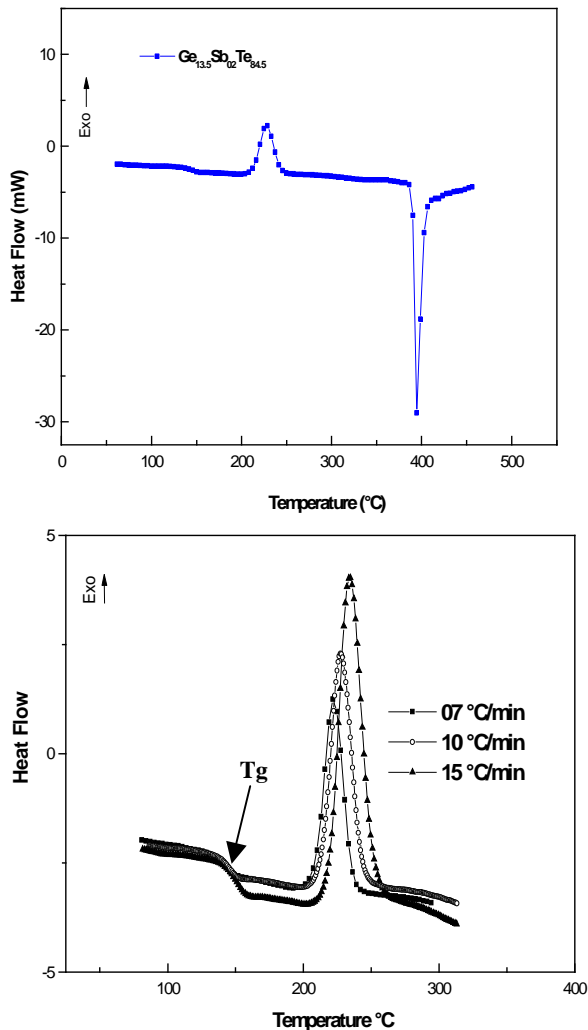


Fig. 4. a- The thermograms of $\text{Ge}_{13.5}\text{Te}_{84.5}\text{Sb}_2$ at rate $10^\circ\text{C}/\text{min}$. b- at different heating rate (7,10,15) $^\circ\text{C}/\text{min}$

In the fabrication of $\text{Ge}_{13.5}\text{Te}_{84.5}\text{Sb}_2$ we changed the diameter of capillary as a result of the modification in the processes of crystallization in $\text{Ge}_{15.5-x}\text{Te}_{84.5}\text{Sb}_x$ ($x = 0.5, 1, 1.5, 2.5$). The role-played by antimony is not clear. The value of the heat capacity of crystallization peak in $\text{Ge}_{13.5}\text{Te}_{84.5}\text{Sb}_2$ is 47 J/g . This value is lower than the value of the total heat capacity in $\text{Ge}_{15.5-x}\text{Te}_{84.5}\text{Sb}_x$ which is 52 J/g [25]. The difference in heat capacity indicates that there is a small number of crystallites. The modification of cooling rate is very important for the phase composition in the glass chalcogenide. We conclude that there is a relation between the rate cooling and the rate of formation of the phases in the glass chalcogenide. The formation of phase

SbTe crystalline gives the possibility to the chains of GeTe to block the tellurium. For this reason we have the same thermal crystallization as in $\text{Ge}_{20}\text{Te}_{80}$ [26]. The change of the cooling rate determines the transformation from $\text{Ge}_{13.5}\text{Te}_{84.5}\text{Sb}_2$ glass to the GeTe glass + crystallites. We have proposed that Te-Te bonds are responsible for the crystallization of GeTe . This consideration is identical for crystallization of SbTe but the position of Te-Te bonds are not the same. The positions of the bonds Te-Te are in the site of the SbTe molecule. The same is valid for GeTe (site of molecule GeTe). If we reduce the quantity of Tellurium connected to the molecule of GeTe and substitute SbTe by Te-Te , a new molecule can be found: GeSbTe ! This has been shown in 1965 by Abrikosov and Danilova-Dobriakova [27]. In the stoichiometric compositions of pseudo-binary line $\text{Ge}_1\text{Te}_7\text{Sb}_4$ $\text{Ge}_1\text{Te}_4\text{Sb}_2$ $\text{Ge}_2\text{Te}_5\text{Sb}_2$, we get the homogenous distribution of Te-Te bonds in the Ge-Sb-Te glass and we equilibrate the formation rate of GeTe glass and SbTe glass during cooling. According to different structural studies using X rays on $\text{Ge}_2\text{Te}_5\text{Sb}_2$ [3, 4, 7, 28] (Table 2) we conclude the structure of $\text{Ge}_2\text{Te}_5\text{Sb}_2$ is cfc in direction of plane (111), (200). We ignored the direction of planes (220), (222), (420). Possibly these atom planes correspond to the oxidation of elements (Te, Sb, Ge) according to XPS analysis [3]. Different bonds exist in $\text{Ge}_2\text{Te}_5\text{Sb}_2$ as evidenced by few studies using EXAFS [3, 5]. In the present stud [20,21] we proposed the structure of $\text{Ge}_2\text{Te}_5\text{Sb}_2$ based on Sb_2Te_3 chains and GeTe_4 chains as shown in Fig. 5. In our model there are two kinds of tellurium bonds: firstly Te-Te bonds in the molecule of Sb_2Te_3 and Te-Te bonds out of molecule of Sb_2Te_3 to connect the molecule of Sb_2Te_3 and GeTe_4 . The first stage in formation of the crystal is the correction of the position of tellurium bonds. The second stage is the formation of the planes Te-Te . These planes are planes of tellurium (Te-Te) in the molecule Sb_2Te_3 . The effect of the construction of these planes is automatically the construction of $\text{Ge}_2\text{Te}_5\text{Sb}_2$ crystal because these plane are connected to Sb , and GeTe_4 . The mechanism of crystallization in $\text{Ge}_2\text{Te}_5\text{Sb}_2$ is based on the percolation from Te-Te bonds (one dimension) to Te-Te-Te plane (two dimension) and the three dimension Te-Sb-Te pyramid and GeTe_4 . This is in a good agreement with Popescu's model [29,30] developed for describing glass-crystal transition in stoichiometric compositions.

Table 2. The different diffraction planes in $\text{Ge}_2\text{Te}_5\text{Sb}_2$ crystal

Reference	CFC	CFC	CFC	CFC	CFC	Film thickness
[4]	111	200	-----	-----	-----	20nm
[28]	111	200	220	-----	-----	100nm
[7]	111	200	220	222	-----	
[3]	111	200	220	222	420	200nm

The first step in the determination of the crystallization parameters, is the verification of the crystalline fraction at maximum peaks which is 0.50. This value indicates in our case there are retarding in crystallization rate. Fig. 6 illustrate the plots $\ln(\alpha/T^{P^2})$ and $\ln(\alpha/T^P - T_0)$ versus $1000/T_P$ the slopes of resulting lines, correspond to the values of energy from Kissinger's model and Augis-Bennett model: to 1.33 eV and 1.30 eV, respectively. The activation energies are the same. Nevertheless the value of E is different from the activation energy of Tellurium in $\text{Ge}_{15.5-x}\text{Te}_{84.5}\text{Sb}_x$ ($x= 0.5, 1, 1.5$)

which is 1.8 eV [20]. The activation energy can also be deduced using equation (28) of Matusita, from slopes of $\ln(-\ln(1-x))$ with $\ln(\alpha)$ at different temperature, 233°C, 234°C, 235°C, 237°C represented in Fig. 7. The value of n equal to 2. In our study we choose m equal to n-1. E is now determined from the slope of plots $\ln(-\ln(1-x))$ with $(1000/T)$ in Fig. 7 which is 2.55 eV. This value is the same as the activation energy of the crystallization of tellurium occurs in one dimension Te-Te in $\text{Ge}_{15.5-x}\text{Te}_{84.5}\text{Sb}_x$ ($x= 0.5, 1, 1.5$) [20].

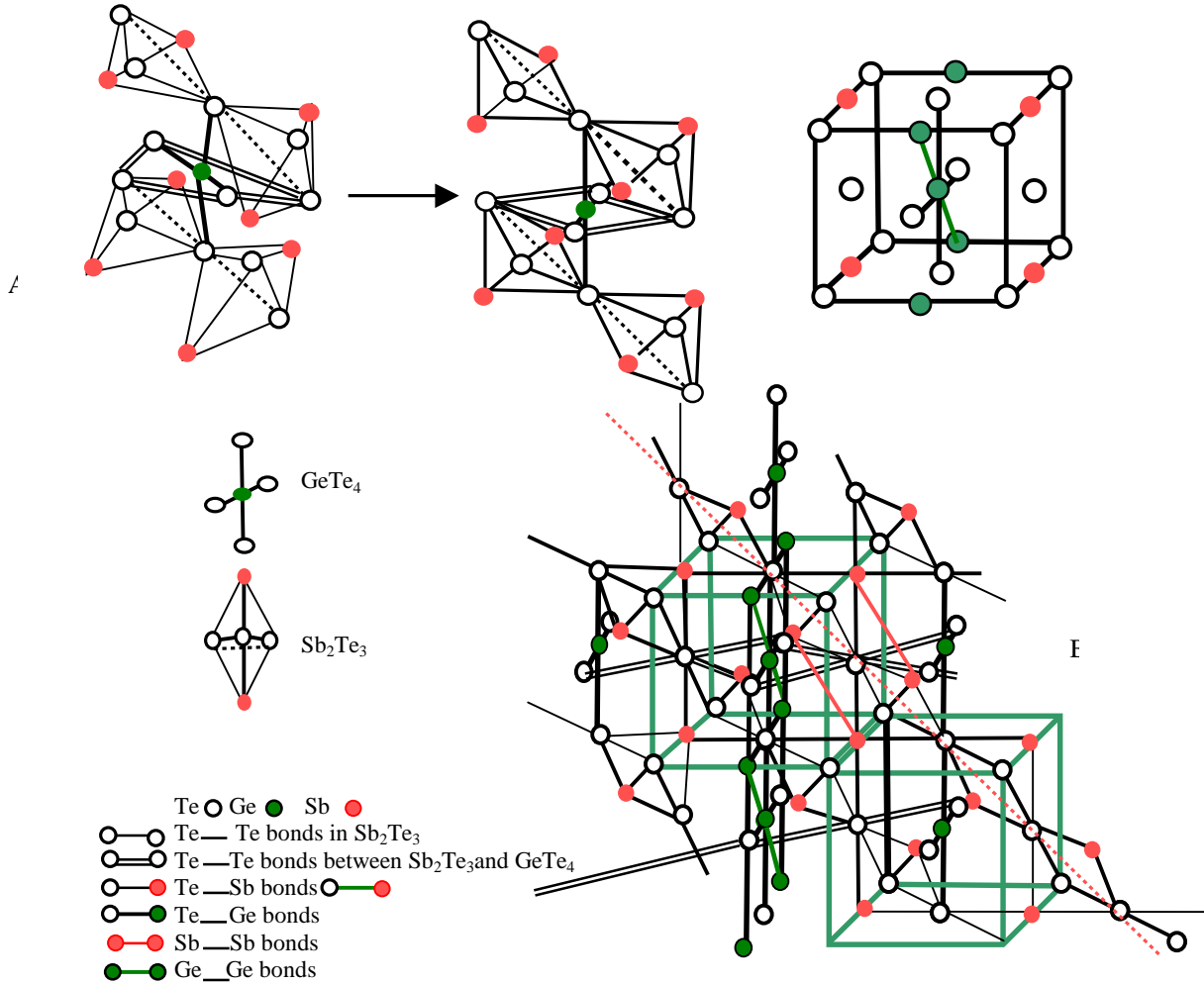


Fig.5. The model of $\text{Ge}_2\text{Sb}_2\text{Te}_3$. A. The transition glass-crystal B. the crystalline structure.

this confirmed the validity of Matusita method in our system. Only the Takhor methods reported the variation of the value of crystallised fraction at maximum of peaks ignoring the time dependence of K in the second differentiation. Augis and Bennet methods generalized this results:

$$x = 0.63 \text{ if } at \gg 1 \text{ and for } at \ll 1 \quad x = 1 - \exp\left(-\frac{n-1}{n}\right)$$

Where n is approximation the activation energy slope of plots of $\ln(\alpha/T^P - T_0)$ versus $1000/T$.

We proposed parameter λ , which has relation with rate cooling, and different phase formed in cooling process as expressed in equation Johnson-Mehl-Avrami in following formula

$$x = \lambda - \exp^{-Kt^n} \quad (29)$$

where $0 < \lambda < 1$

The derivation of eqs (29) yields the usual rate equation for growth processes

$$\frac{dx}{dt} = (\lambda - x)nK^n t^{n-1}(1 + at) \quad (30)$$

Where $at = \frac{\alpha Et}{RT^2}$ using eqs (1) and the approximation that $T \gg T_0$, the expression $at \approx \frac{E}{RT}$.

For a chalcogenide glass $E \gg RT$ because the evaluation of $RT \approx 10^{-2} eV$ and $E \approx eV$ i.e $at \gg 1$ the eqs (30) becomes

$$\frac{dx}{dt} = (\lambda - x)nK^n t^{n-1} \left(\frac{E}{RT} \right) \quad (31)$$

Derivation of eqs (31) leads to

$$\frac{d^2x}{dt^2} = (\lambda - x)nK^n t^{n-2} \left(\frac{E}{RT} \right) \left(n \left(1 + \frac{E}{RT} \right) - 2 - nK^n t^n \left(\frac{E}{RT} \right) \right) \quad (32)$$

This is converted to

$$\frac{d^2x}{dt^2} = (\lambda - x)n^2 K^n t^{n-2} \left(\frac{E}{RT} \right)^2 \left(1 - K^n t^n \right) \quad (33)$$

The highest growth rate of the crystalline fraction at the temperature peak T^P

$$\frac{d^2x}{dt^2} = (\lambda - x)n^2 K^n t^{n-2} \left(\frac{E}{RT^P} \right)^2 \left(1 - K^n t^n \right) = 0 \quad (34)$$

can be written as

$$Kt^n = 1 \quad (35)$$

In logarithm form $\ln K_0 - \frac{E}{RT^P} + \ln \frac{T^P - T_0}{\alpha} = 0$ (36) it

similar to the equation (21) of Augis and Bennett, using the approximation $T^P \gg T_0$ eqs 36 becomes

$$\ln K_0 - \frac{E}{RT^P} + \ln \frac{T^P}{\alpha} = 0 \quad (37)$$

From Fig. 6 the plot of $\ln(\alpha/T^P)$ versus $(1000/T)$ the slope obtained is E is equal to 1.35 eV. If $\lambda = 1$ the chalcogenide glass is 100 %. Replacing eqs (35) in eqs (29) the fraction crystallized at T^P is 0.63 is revealed by two peaks of compositions $Ge_{15.5-x}Te_{84.5}Sb_x$ ($x = 0.5, 1, 1.5$) [20] and one peak of composition $Ge_{20-x}Te_{80}Sb_x$ ($x = 0.3, 4.5$) [31].

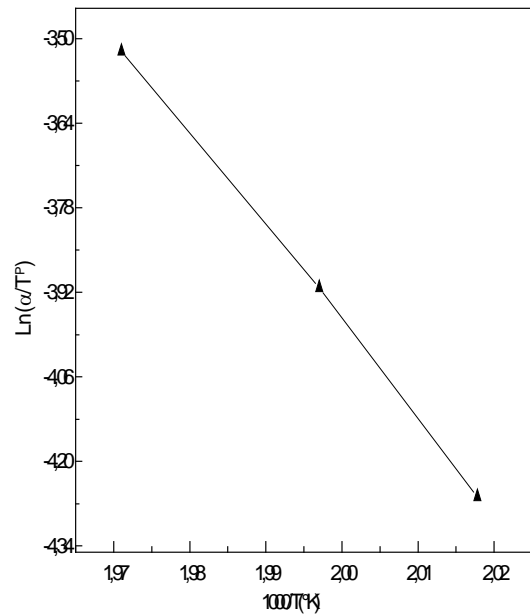
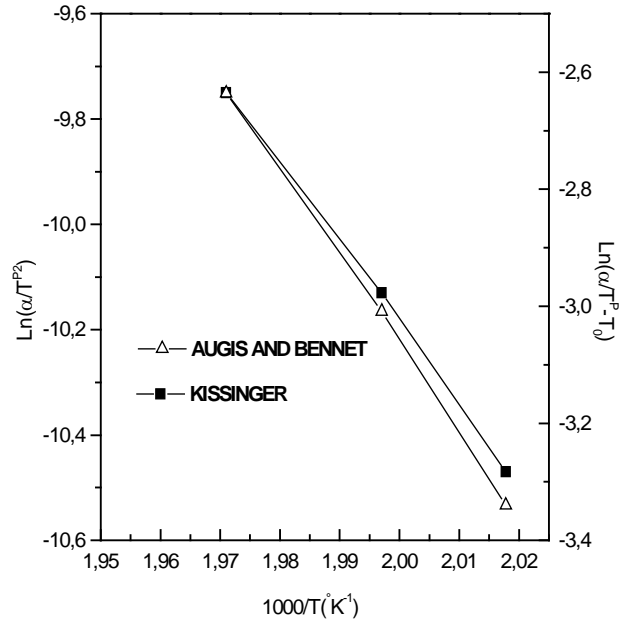


Fig. 6. The variation of $\ln(\alpha/T^P^2)$, $\ln(\alpha/T^P - T_0)$ and $\ln(\alpha/T^P)$ as a function of $(1000/T^P)$

For $0 < \lambda < 1$ the chalcogenide glass contains a fraction of crystal, x^P , as expressed by $x^P = \lambda - 0.368$ (38). The presence of exothermic peak in DSC thermograms shows the presence of crystallization phenomenon i.e the existence of x^P . However x^P is defined for $0.368 < \lambda < 1$. We conclude that the minimum amount of glass in chalcogenide glass is superior for 0.368 % and the maximum amount of crystal in chalcogenide glass is inferior to 0.632 %.

The volume fraction at T^P can be obtained from DSC curve by using $x^P = \frac{H_p}{H_{total}}$, For our case the value of x^P is

0.50 According to eq. (38) $\lambda = 0.868$. We conclude that 13 % of composition $Ge_{13.5}Te_{84.5}Sb_2$ is crystallized during the cooling process. We can explain the slow crystallization phenomenon in glass phase residue by two kind of morphologic obstacles: firstly crystallites of another phase for example crystallites of SbTe in tellurium, secondly crystallites of the same phase. As an important observation, in the chalcogenide glass there are chains of tellurium but these chains are different in length as a result of the cooling of the rate process.

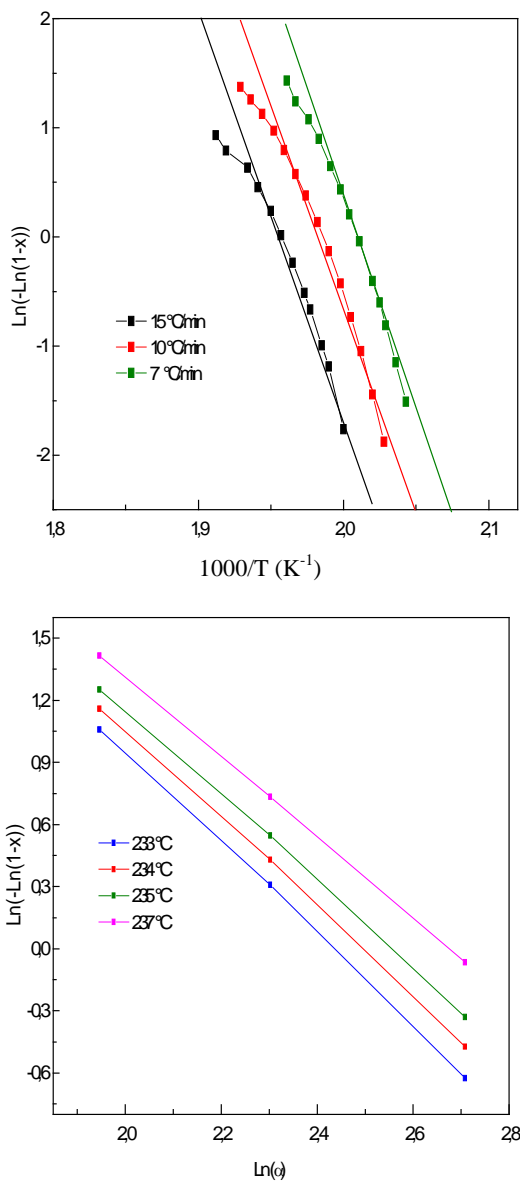


Fig.7. The variation of $Ln(\alpha)$ and $(1000/T)$ as a function of $Ln(-Ln(1-x))$

The formation of identical tellurium chains is not possible. Short chains are formed. For short chains of crystallites, the amount of order is lower. This explains the decrease of the activation energy of tellurium from 1.8 eV[20] to 1.35 eV.

5. Conclusions

From our study and different models proposed with the aim to explain the crystallization process in chalcogenide GeSbTe, and by using the modification of Johnson-Mehl-Avrami to

$$x = \lambda - \exp -Kt^n$$

where

$$0.368 < \lambda \leq 1$$

we conclude that

- the existence of Te-Te bonds in chalcogenide liquids is responsible for the formation of chalcogenide glass due to specific physical properties of hybridized bonds Te-Te as a consequence of the appearance of exciton pair of $Te^{n+} - e^-$.
- the presence of T_g in thermograms of DSC is insufficient for definition of glass chalcogenide, we must verify the crystalline fraction at the maximum of the exothermic peak of crystallization. If x is equal to 63% we have 100% glass and for x different from 63% we have glass chalcogenide plus crystallites.
- the crystallization process starts in a particular region which includes high disorder in chalcogenide glass and the existence of ordered regions (crystallites) causes an obstacle for crystallization.
- the composition of glass chalcogenide glass changes with cooling rate as a consequence of the change in the crystallization process.

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