THE METHODS MATUSITA, KISSINGER AND OZAWA IN THE STUDY OF THE CRYSTALLIZATION OF GLASSES. THE CASE OF Ge-Sb-Te ALLOYS

L. Heireche, M. Belhadji
Physics Department, ES-Senia University, BP1524 El M'Naouer Oran, Algeria.

Chalcogenide glasses based on Ge-Te-Sb are used in the technology of phase change optical memories. Non-isothermal crystallization for $Ge_{15.5-x}Te_{84.5}Sb_x$ (0.5 <x< 1.5) investigated by differential scanning calorimetry (DSC) shows two glass transition temperatures followed by two crystallization peaks and melting point at 385°C . The activation energy of crystallization has been calculated in the frame of three models: Matusita, Kissinger and Ozawa. The particularity of every model is analysed.

1. Introduction

The ovonic chalcogenide glasses have important applications. One of most important properties of some chalcogenide glasses with tellurium is the optical and electrical switching between two states : the amorphous and the crystalline one [1-3]. The understanding of the phase transition in chalcogenides is crucial for applications in simple or multistage memories, whose pioneer is S. R. Ovshinsky from ECD, USA [4-11]. In a previous paper [12] we have determined the kinetic crystallization parameters of $Ge_{20}Te_{80}$ binary eutectic and $Ge_{20-X}Te_{80}Sb_X$ ternary eutectic. The crystallization of glassy alloys of composition $Ge_{15.5-x}Te_{84.5}Sb_x$ (0.5 <x< 1.5) has been previously investigated [13]. In this paper we discuss the methods used for getting the activation energy of crystallization.

2. Matusita's method

The Matusita model evidences the importance of the factor m/n for the determination of the activation energy of the crystallization process. This fact is related to the nucleation and growth of the crystallites in the amorphous matrix.
The equation of Matusita has the following form :

$$\ln \alpha = -1.052 \left(\frac{m}{n} \right) \left(\frac{E}{RT} \right) - \left(\frac{1}{n} \right) \ln \left(-\ln(1-x) \right) + cste .$$ (1)

Starting from this equation we succeeded to calculate the kinetic paramaters of crystallization, the characteristic of the nucleation, n, the factor m that represents the dimension where the growth is embedded and the values of the activation energies, E_a, of the investigateed materials.
The plots of the *Ln(-Ln(1-x))* versus temperature in an Arrhenius coordinates are shown in Figs. 1-3 for both phases evidenced on the differential scanning calorimetry curves.
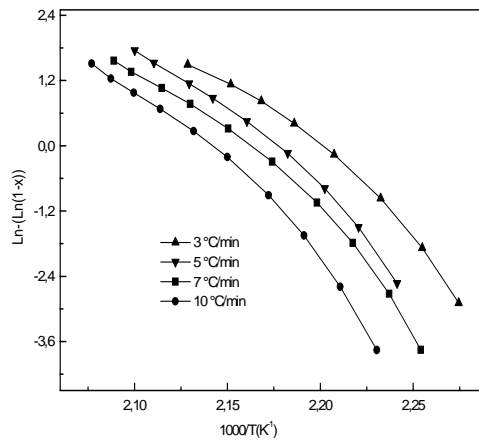a- $Ge_{15}Sb_{0.5}Te_{84.5}$
The first phase

Fig. 1 The variation of Ln(-Ln(1-x)) as a function of 1000/T.
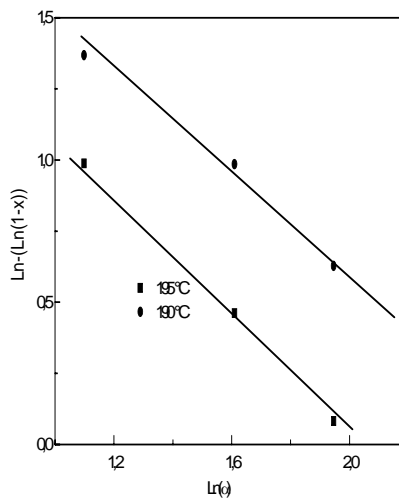
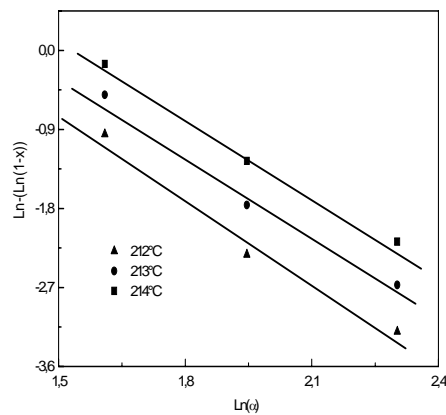*Fig. 2. The variation of Ln(-Ln(1-x)) as a function of Ln(α).*

The second phase

Fig. 3 The variation of Ln(-Ln(1-x)) as a function of Ln(α).
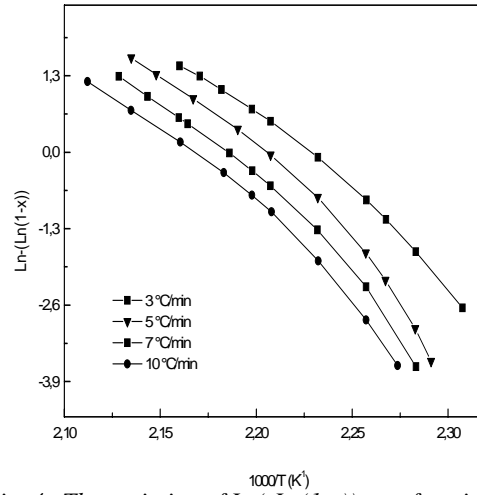
Fig. 4. The variation of Ln(-Ln(1-x)) as a function of 1000/T.

b- Ge$_{14.5}$Sb$_{01}$Te$_{84.5}$
The first phase
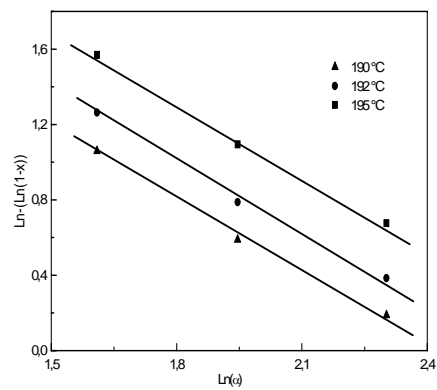
Fig. 5. The variation of Ln(-Ln(1-x)) as a function of Ln(α).

The second phase

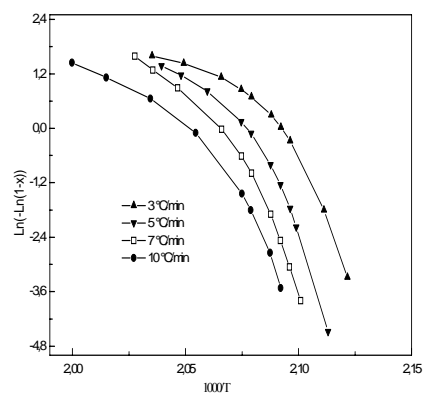*Fig. 6. The variation of Ln(-Ln(1-x)) as a function of 1000/T.*

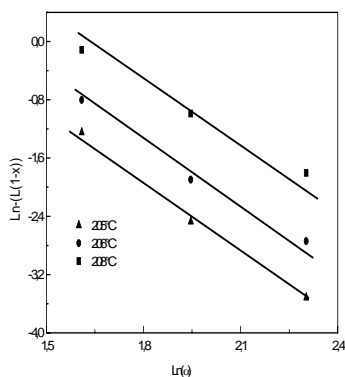*Fig. 7. The variation of Ln(-Ln(1-x)) as a function of Ln(α).*

The curves of ln (-ln (1-x)) as a function of lnα for two isotherms, well defined, are represented on the previous figures. The slope furnish the value of the index n for every sample. The choice of the isotherms is arbitrary, but we have preferred the values situated at high temperatures (quasi-complete crystallization).

The curves ln (-ln (1-x)) as a function of 1000/T for various annealing rates α are represented on the previous figuresfor allthe samples investigated. The slopes of these curves give the value of the energy of activation for the crystallization E_a.

Starting from the graphs ln (-ln (1-x)) versus 1000/T for various speed of heating, α, one can remark that the slopes are independent of the heating rate. We have, therefore, calculated the mean value of E_a for every heating speed.

It is remarkable that the first peak exhibits one single slope. The second peak exhibits two slopes. In our calculation is taken into account only the first slope because the second one corresponds to around 97 % crystalline fraction in the material.

Table 1 shows the values of the indices n, m and the value of the activation energy, E_a, for different samples $Ge_{15.5-x}Te_{84.5}Sb_x$ (0.5<x<1.0).

Table 1 The thermal parameters of the first peak.

Composition	n	m	E_a (kJ/mol)	E_a (eV)
$Ge_{15}Sb_{0.5}Te_{84.5}$	0.97=1	1	239.95 $\pm$ 2	2.49 $\pm$ 0.02
$Ge_{14.5}Sb_{01}Te_{84.5}$	1.20=1	1	241.36 $\pm$ 1.82	2.50 $\pm$ 0.02

Table 2 The thermal parameters for the second peak.

Composition	n	m	E_a (kJ/mol)	E_a (eV)
$Ge_{15}Sb_{0.5}Te_{84.5}$	3.09=3	3	310.84 $\pm$ 6.84	3.22 $\pm$ 0.07
$Ge_{14.5}Sb_{01}Te_{84.5}$	2.61=3	3	303.98 $\pm$ 9.18	3.15 $\pm$ 0.09

3. Kissinger's method

The Kissinger model has been established, also, in dynamical regime. As opposite to the model of Matusita, it is considered that on the top of crystallization peak the amount of crystallized fraction is x=0.63.
The Kissinger equation has the form:

$$\ln\left(\frac{\alpha}{T_p^2}\right) = \frac{-E_a}{kT_p} + \ln\left(\frac{RC_0}{E_a}\right) \qquad (2)$$

where T_p is the temperature corresponding to the top of the crystallization peak.
The curves of Ln (α/T_0^2) as a function of $1000/T_0$ are represented in Figs. 8 and 9.
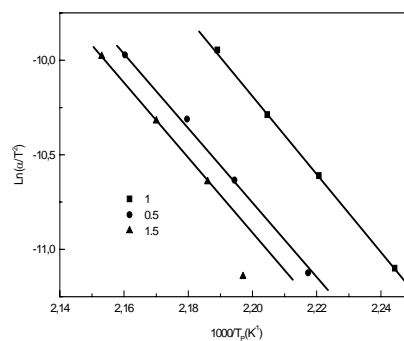
Fig. 8. The variation of Ln(α/T^2) as a function of $1000/T_p$ for the first phase.
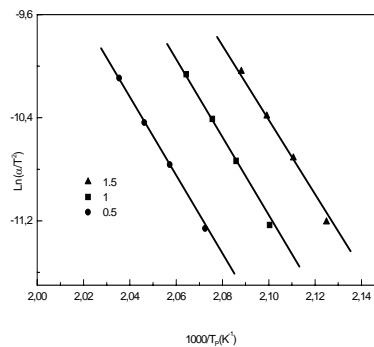
Fig. 9. The variation of Ln(α/T^2) as a function of $1000/T_p$ for the second phase.

Table 7. The thermal parameters for the first crystallization peak.

Composition	E_c (KJ/mol)	Ec (eV)
$Ge_{15}Sb_{0.5}Te_{84.5}$	170.72 ±5.78	1.75± 0.06
$Ge_{14.5}Sb_{01}Te_{84.5}$	172.68±1.93	1.79 ± 0.02
$Ge_{14}Sb_{1.5}Te_{84.5}$	166.89 ±0.96	1.73 ± 0.01

Table 8 The thermal parameters for the second peak.

Composition	E_c (KJ/mol)	Ec (eV)
$Ge_{15}Sb_{0.5}Te_{84.5}$	260.47±2.90	2.70 ± 0.03
$Ge_{14.5}Sb_{01}Te_{84.5}$	270.12±4.82	2.80 ± 0.05
$Ge_{14}Sb_{1.5}Te_{84.5}$	262.40±6.80	2.72 ± 0.07

4. Ozawa's method

As remarked before, by supposing that at the maximum of the crystallization peak corresponds a crystalline fraction of x~0.63, Ozawa proposed the following relation to be valid :

$$\ln \alpha = - {E_a}\big/{RT_P} - + \ln\left({C_0 E_a}\big/{R} \right) + const \tag{3}$$

The curves of lnα as a function of $1000/T_0$ are represented on the Figs. 10 and 11.

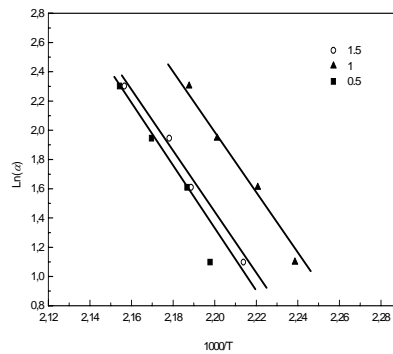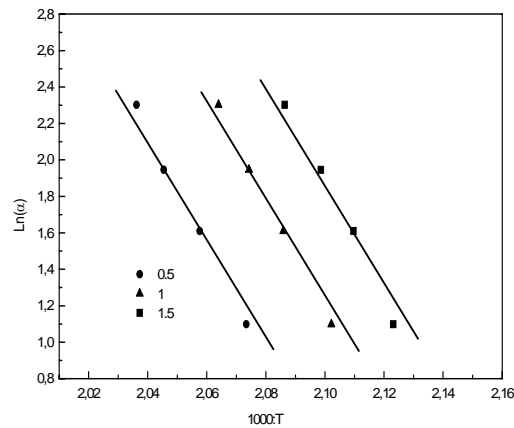*Fig. 10 The variation of Ln (α) as a function of 1000/T.*

Fig. 11. The variation of Ln (α) as a function of 1000/T for the second phase.

Table 9. The values of the activation energy of crystallization for the first peak.

Composition	E_a (kJ/mol)	E_a (eV)
$Ge_{15}Sb_{0.5}Te_{84.5}$	190.00 ± 1.60	1.97 ± 0.02
$Ge_{14.5}Sb_{01}Te_{84.5}$	178.17 ± 1.60	1.84 ± 0.02
$Ge_{14}Sb_{1.5}Te_{84.5}$	177.13 ± 0.98	1.83 ± 0.01

Table 10 The values of the activation energies for the second peak.

Composition	E_a(kJ/mol)	E_a (eV)
$Ge_{15}Sb_{0.5}Te_{84.5}$	264.65 ± 1.23	2.74 ± 0.01
$Ge_{14.5}Sb_{01}Te_{84.5}$	259.90 ± 0.66	2.69 ± 0.01
$Ge_{14}Sb_{1.5}Te_{84.5}$	271.20 ± 1.57	2.82 ± 0.02

The study of the crystallization kinetics of the vitreous materials $Ge_{15.5-x}Te_{84.5}Sb_x$ (x = 0.5, 1, 1.5) allowed to estimate the parameters that govern the crystallization process, among these the index n and the activation energy E_a. This study can be achieved in isothermal regime or in dynamical regime. We have decided to use the dynamic mode that permitted to follow the evolution of the investigateed samples as a function of temperature.

The study is carried out by the Matusita's method. Matusita opposes his method to the traditional methods for the treatment of the crystallization kinetics in the dynamic mode, as done by the models of Kissinger and Ozawa. These are based not only on the JMA equation proposed in isothermal regime, but, also, on the approximations as e.g. those taking into account the value $x_p = 0.63$ of the crystallized fraction at the top of the crystallization peak.

The Matusita's model points out the importance of the factors n and m, which represent the nucleation and growth and takes into account these factors in the estimation of the activation energy of the crystallization process.

By applying this method, we succeeded to get the nucleation modes, the dimension that corresponds to the growth, as well as the values of the activation energy of the investigated materials.

The nucleation is produced according to different mechanisms that correspond to n = 1 and n = 3, respectively, for the first and second phase. The values m=n have been considered because the number of nuclei grows with the temperature. The growth is one-dimensional for the first phase and three-dimensional for the second phase.

Starting from these results, we have observed that the addition of antimony does not influence the activation energies. They remains the same : 2.5 eV and 3 eV for the first and sefcond peak.

The results obtained by the Kissinger method seems to be in good agreement with the results got by Ozawa's method. It is remarkable that the energy values for the two phases are independent of antimony content and are 1.8eV and 2.7 eV, respecively.

Several hypotheses have been introduced in order to understand the role played by antimony. The most interessant hypothesis is that of Moss et DeNeufville [15] The authors suppose that antimony is captured in the $GeTe_4$ tetrahedron, and, as a consequence, Sb will prevent the breaking of the Ge-Te bonds and will slow down the crystallization of the remaining phase.

5. Theoretical hints

The study of crystallization kinetics in glass-forming liquids under non-isothermal conditions are of two types. The first one is based on Johnson–Mehl–Avrami [14-15] (JMA) equation of isothermal transformation kinetics:

$$x(t) = 1 - \exp\left(-Kt^n\right)$$

(4)

where x(t) is the volume fraction of the initial material transformed at time t, n is the Avrami exponent (the exponent which reflects the nucleation rate and the growth morphology) and K is the reaction rate constant to which an Arrhenian temperature dependence is usually assigned:

$$K = K_0 \exp\left(-E_a / kT\right)$$

(5)

In this equation, E_a is the activation energy for the crystallization reaction, which describes the overall crystallization process, k_B is the Boltzmann constant, T is the isothermal temperature, and K_0 is the frequency factor. The theoretical basis for interpreting the DSC results are Kissinger[16] and Ozawa[17] methods as calculated according to JMA theory and using the highest rate of a transformation at maximum peak approximations interpreted in this equations, respectively :

$$\ln\left(\alpha / T_P^2\right) = -E_a / kT_p + const$$

(6)

$$\ln\left(\alpha\right) = -E_a / kT_p + const$$

(7)

where T_p is temperature at maximum peak $\alpha = dT/dt$ is heating rate and E_a is activity energy. However, Matusita [18-21] model is specifically for non-isothermal crystallization in which the crystallized fraction(x) can be described as a function of time t according to the following formula:

$$\ln\left(-\ln\left(1-x\right)\right) = -n \ln \alpha - 1.052\left(mE / RT\right) + const$$

(8)

where n and m represent process of crystallization, when the number of nuclei is inversely proportional to the heating rate, m is equal to n-1, if the number of nuclei does not change with the heating rate m = n. The value of n for various crystallization mechanisms are summarized in Table 11.

Table 11. Values of m for different crystallization mechanism

Crystallization mechanism	m
Three-dimensional growth	3
Two-dimensional growth	2
One-dimensional growth	1
Surface nucleation	1

6. Discussion and conclusions

The thermal DSC and X-ray diffraction (Fig. 12) of the peritectic composition $Ge_{15}Te_{84.5}Sb_{0.5}$ show the presence of phase separation between the tellurium and the tellurium + GeTe matrix.The tellurium precipitates in the hexagonal phase, and is managed by the nucleation process at vitreous transition T_{g1} (120°C) , this phenomenon is observed in eutectic composition $Ge_{15}Te_{85}$ heated at 5°C/min, which is characterized by T_g (120°C) followed by two peaks of crystallization T_{c1} and T_{c2} (182°C, 207°C). However, the precipitation of the tellurium in $Ge_{20}Te_{80}$ does not show

separation,which is characterized by T_g (146°C) followed by only one peak of crystallization, T_{c1} (205°C) [24,25].
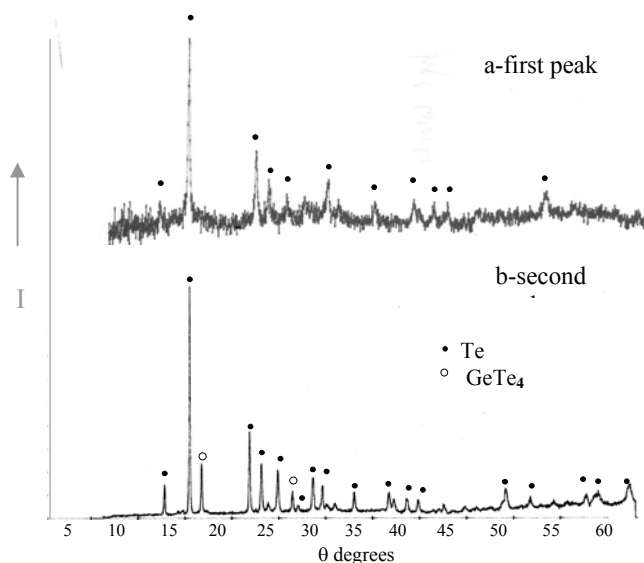

Fig. 12. X-ray diffraction patterns of the composition $Ge_{15}Te_{84.5}Sb_{0.5}$.

The explanation for the observed crystallization phenomena in Ge-SbTe alloys is that GeTe creates an obstacle to the nucleation of tellurium. For this reason, it appears the second nucleation point, T_{g2}, at 146°C. It provokes the precipitation of tellurium in the hexagonal phase, because the T_{g1} and T_{g2} show a similar rate of nucleation. This could explain the vitreous transition in binary $Ge_{15}Te_{85}$ evidenced through an endothermic peak with an important area [24]. The crystallization of GeTe is a consequence of the precipitation of tellurium (second peak) because there are bonds between the tellurium and telluride. In this case we note that the two crystallization peaks are separated when the antimony percent increases and germanium decreases causing a small overlapping between crystallization peaks in $Ge_{14.5}Te_{84.5}Sb_{01}$, which increases in $Ge_{14}Te_{84.5}Sb_{1.5}$ as can be seen on the DSC curves. If the amount of antimony increases the two peaks unite and become only one peak that starts at T_{c1}. Meantime the T_{g2} disappears. This facts can be explained as follows: The quantity of tellurium trapped by GeTe is released because, firstly, the reduction in germanium and then because the antimony is trapped by GeTe. This is conditioned by the fact that there are not Ge-Sb bonds according to EXAFS on Ge [26]. There are only Te-Sb bonds formed in Ge-Te-Sb Fig. 13 describes the crystallization process and the role played by antimony in the vision of the authors of this paper.
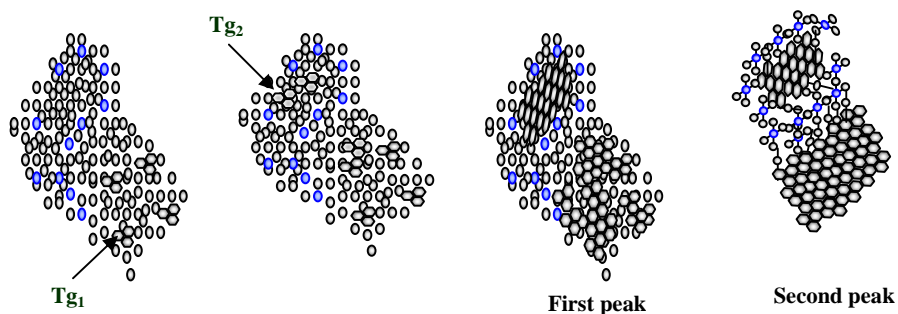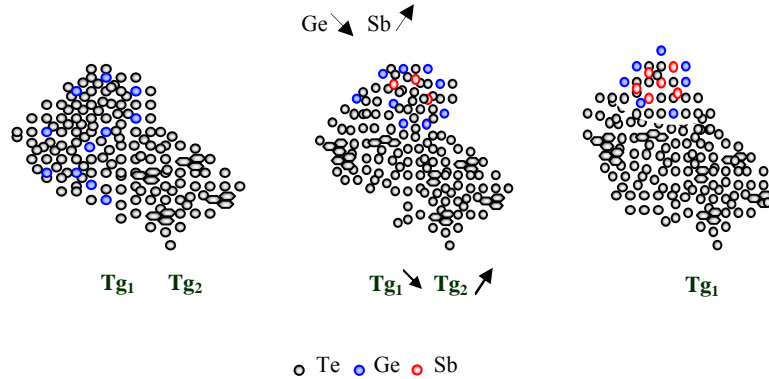
Fig. 9. The role played by Sb in the crystallization process of $Ge_{15}Te_{85}$.

The values of the activation energies of crystallization for $Ge_{15}Te_{84.5}Sb_{0.5}$ using Kissinger and Ozawa methods for tellurium and tellurides are 1.8 eV and 2.7 eV, respectively, both values of the energies are the same obtained for the composition $Ge_{14.5}Te_{84.5}Sb_{01}$ and $Ge_{14}Te_{84.5}Sb_{1.5}$. We conclude that these last compositions can be identified identification with the structure of $Ge_{15.5}Te_{84.5}Sb_{0.5}$. In general, the energies of activation obtained by the Kissinger's method for compositions with high concentration of tellurium as in the case of $Ge_{20}Te_{80}$ [12, 27], $Ge_{17}Te_{80}Sb_{03}$, $Ge_{16}Te_{80}Sb_{04,}$ $Ge_{15}Te_{80}Sb_{05}$ [12], are equal to 1.8 eV. This value represents only the activation energy of the precipitation of hexagonal tellurium. Are there crystallization peaks corresponding to phases which are not visible on the DSC thermograms ? The activation energy for crystallization was also calculated according to Matusita's model, which gives (for m) 2.4 for tellurium and 3 for GeTe. We can observe from Matusita, Kissinger and Ozawa models that always the activation energy of tellurium is above that of GeTe because the crystallization occurs in one-dimensional process in tellurium (Te-Te) and in a three-dimensional process in GeTe. This fact confirmed that the crystallization occurs by addition of $GeTe_4$ tetrahedra to the cubic phase of GeTe (a similar observation has been made by Saiter [29]). From the results of the study of the crystallization kinetics in glassy $Ge_{15.5-x}Te_{84.5}Sb_x$ (0.5 <x< 1.5) alloys by three different methods under non - isothermal condition and by comparing with the results of other authors we can conclude that in all the glasses in the ternary system Ge-Te-Sb and binary GeTe system, with high tellurium content, the crystallization is done by the precipitation of tellurium in the hexagonal phase.

References

 [1] S. R. Ovshinsky, Phys. Rev. Lett. **21**, 1450 (1968).
 [2] S.R. Ovshinsky, H. Fritzche, Metallurgical Transactions **2**, 641 (1971).
 [3] S. R. Ovshinsky, P. H. Klose, J. Non-Cryst. Solids, **8-10**, 892 (1972).
 [4] N. Yamada, E. Ohno, K. Nishiuchi, N. Akahira , J. Applied Physics. **69**(5), 2849 (1991).
 [5] J. Colmenero and J. M. Barandiaran, J.non-Cryst.Solids, **30**, 263 (1979).
 [7] J. R. Boonell and C. B. Thomas, Solid State Electron, **15**, 1261 (1972).
 [8] C. B. Thomas, A. Feltz, J.Non-Cryst. Solids **86**, 41 (1986).
 [9] C. B. Thomas, A. Feltz, J. Non-Cryst.Solids, **86**, 33 (1986).
[10] S. Asokan, G. Parthasarathyand, E. S. R. Gopal, J.Non-Cryst.Solids, **86**, 48 (1986).
[11] J. Cornet, Ann.Chim, **10**, 239 (1975).
[12] N.Ziani, M. Blhedji, L. Heireche, Z. Bouchour and Blebachir , Physica B **358**, 132 (2005).
[13] L. Heireche, M. Belhadji, Journal of Ovonic Research **2**(6), 119 (2006).
[13 bis]   L. Heireche, M. Belhadji, Journal of Ovonic Research **2**(6), 125 (2006).
[14] W.A. Johnson, R.F. Mehl: Trans. Am. Inst. Min. (Metall.) Eng. (1939)**135**,416
[15] M. Avrami: J. Chem. Phys. **7**, 1103 (1939); **8**, 212 (1940); **9**, 177 (1941)

[16] H. E. Kissinger: Anal. Chem. **29**, 1702 (1957).

[17] T. Ozawa, J. Thermal. Anal. **2**, 301 (1970).

[18] K. Matusita, S. Sakka, Bull. Inst. Chem. Res. Kyoto Univ **59**, 159 (1981).

[19] S. Mahadevan, A. Giridhar, A.K. Singh, J. Non-Cryst.Solids **88**, 11 (1986).

[20] K. Matusita, T. Komatsu, R. Yokota, J. Mater. Sci. **19**, 291 (1984).

[21] N. Rysava, T. Spasov, L. Tichy, J. Therm. Anal. **32**, 1015 (1987).

[22]M. Belhadji ,N.Ziani and M.Mostefa Chinese J .Physics vol. 43,NO.1-I

[23] S.C.Moss and J.P.DeNeuville Mat.Research Bul, **7**, 423 (1972)

[24] J. A. Savage, J.Non-Crystalline Solids, **11**, 121 (1972).

[25] M.A. Abdel-Rahim, A.Y. Abdel-Latief, A.S. Soltan, M.Abu El-Oyoun, Physica
B **322**, 252 (2002).

[26] J. M.Saiter, Q. Ma, S.Bénazeth, M. Belhadji, C. Vautier, Matetials Letters **19**, 287 (1994).

[28] A. A. Abu-sehly, Physica B **325**, 372 (2003).

[29] J. M. Saiter J. Optoelectron. Adv. Mater. **3**(3), 685 (2001).