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# NON - ISOTHERMAL CRYSTALLIZATION IN $Ge_{15.5-x}Te_{84.5}Sb_x$ (0.5 <x< 1.5)

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Chalcogenide glasses based on Ge-Te-Sb are used in the technology of phase change optical memories. A study of non-isothermal crystallization for $Ge_{15.5-x}Te_{84.5}Sb_x$ (0.5 <x< 1.5) by differential scanning calorimetry (DSC) show two glass transition temperatures followed by two crystallization peaks and melting point at 385°C . The phase separation in crystallization process corresponds to the precipitation of tellurium in the hexagonal form. The crystallization activation energies of tellurium and GeTe have been determined under dynamics conditions using Kissinger's model and the results are 1.8 eV and 2.7 eV, respectively. The agreement between Kissinger's model and Ozawa's model was demonstrated.

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*Keywords*: Ge-Te-Sb, Phase change memory material, Ovonic material, Crystallization, Activation energy of crystallization

## 1. Introduction

One of the most important discovery in modern technology is the phase change memory in chalcogtenide glasses. This was made by Ovshinsky [1-3] in the ternary and quaternary glasses. Glasses from the system Ge-Te-Sb have been successfully used in this application [4] by exploiting the optical and thermal properties of glass-crystal transition [5-11]. The study of the thermal, electric and optical parameters of Ge-Te-Sb allowed to control the physical properties of the transition from glass to crystal. In our 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.These alloys exhibit one glass transition temperature followed by one crystallization temperature. This paper deals whith the study of $Ge_{15.5-x}Te_{84.5}Sb_x$ (0.5 <x< 1.5) alloys which exhibit such a behaviour. The studied compositions correspond to the transitory ternary peritectics evidenced by Legendre et al [13].

## 2. Experimental

The preparation of the samples was carried out in two steps. First, the three elements (99.999 % purity) in suitable quantity are introduced into a quartz ampoule and sealed in vacuum of $10^{-5}$ Pa. Then the ampoules were heated up to the melting of the components and quenched in air. The compositions of the bulk alloys was checked by atomic absorption spectrometry (Perkin Elmer 2380 apparatus). 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 was checked by X-ray diffraction. The thermograms were recorded using a Setaram DSC92 at various heating rates(3, 5, 7,10 K/min).

## 3. Theoretical analysis

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

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

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/or the growth morphology) and *K* is the reaction rate constant to which an Arrhenian temperature dependence is usually assigned:

$$K = K_0 \exp\left(-{E_a}\big/{kT}\right) \tag{2}$$

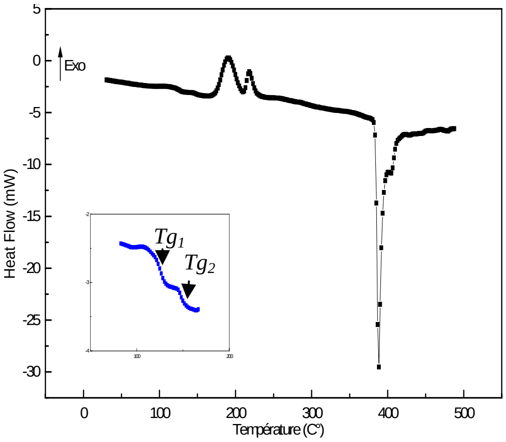

*Fig. 1. DSC trace of Ge15.5Te84.5Sb0.5 heated at 10$^{o}$C/min.*

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 and the calculations were performed according to JMA theory and using the highest rate of a transformation at maximum peak approximations interpreted in these equations, respectively :

$$\ln\left({T^2}\big/{\alpha}\right) = -{E_a}\big/{RT_P} + const \tag{3}$$

$$\ln\alpha = -{E_a}\big/{RT_P} + const \tag{4}$$

where $T_p$ is temperature at the peak, α =dT/dt is the heating rate and $E_a$ is the activation energy. However, Matusita's model [18-21] is appropriate for non-isothermal crystallization in which the crystallized fraction(x) can be described as a function of time t according to the following formula:

$$\ln\left(-\ln(1-x)\right) = -n\ln\alpha - 1.052\left({mE}\big/{RT}\right) + const \tag{5}$$

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

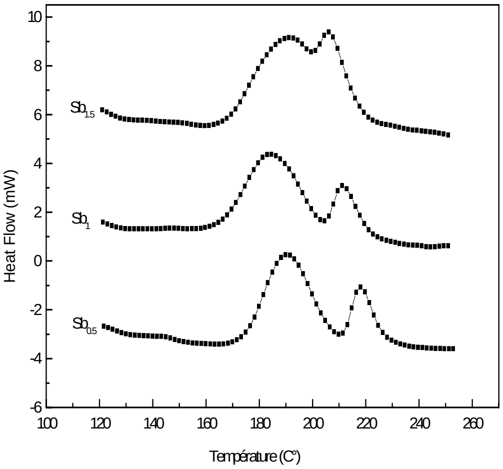

*Fig. 2. Crystallization peaks for three comoposition at 10°C/min.*

*Table 1 Values of m for different crystallization mechanisms*

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

## 4. Results

Fig 1 shows a typical DSC curve obtained when the chalcogenide $Ge_{15}Te_{84.5}Sb_{0.5}$ was heated at a constant rate of 10 °C/min. Five characteristic features are observed in the studied temperature range. The first $T_{g1}$ and second $T_{g2}$ correspond to the glass transition temperatures. They are followed by two exothermal peaks characteristic to two crystallization temperatures $T_{c1}$, $T_{c2}$ and last temperature corresponding to the strong endothermal peak represent the melting point. The same process were observed for the compositions $Ge_{14.5}Te_{84.5}Sb_{01}$ and $Ge_{14}Te_{84.5}Sb_{1.5}$ in Fig 2. The exact temperatures are given in table 2.

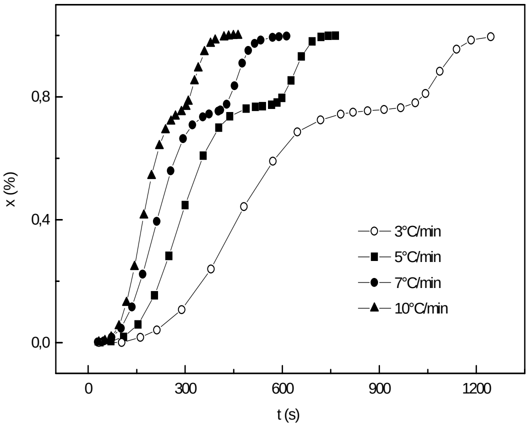

*Fig. 3 Curves of non-isothermal crystallization process of $Ge_{15.5}Te_{84.5}Sb_{0.5}$*

*Table 2. Glass transition, crystallization temperature and melting temperatures in °C.*

| X | 0.5 | 1 | 1.5 |
|---|---|---|---|
| $T_{g1}$ | 122 | 117 | 115 |
| $T_{g2}$ | 145 | 147 | 151 |
| $T_{c1}$ | 174 | 166 | 168 |
| $T_{c2}$ | 210 | 203 | 199 |
| $T_f$ | 384 | 385 | 386 |

Fig 3 shows the non-isothermal curves of crystallized fraction x vs time t of $Ge_{15.5}Te_{84.5}Sb_{0.5}$ at deferent heat rates. Those plots confirmed the present of two crystallisations process correspond tow exothermic peaks. In present work we have been calculated the activation energy for each peaks where $x=S/S_T$ , the crystallized fraction x at a given temperature T which $S_T$ is the total area of the exothermic peak and S is area between $T_0$;where the crystallization starts and $T_f$ where the crystallization completes of peak.

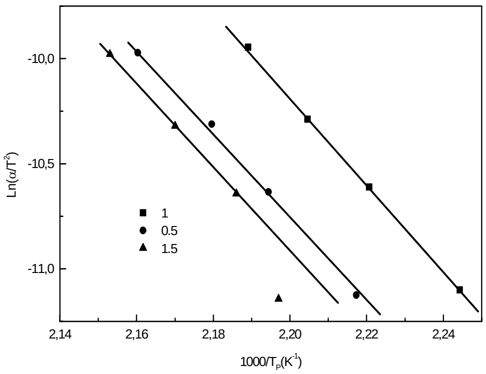

*Fig. 4. The plots $Ln(\alpha/T^2)$ versus $1000/T_0$.*

Fig 4 a, b illustrate the plots $Ln(\alpha/T^2)$ versus $1000/T_0$ the slopes of the resulting lines, correspond to the values of energy from Kissinger's model of first and second peaks for three compositions. Similarly Fig 5 a,b illustrates the plots $Ln(\alpha)$ versus $1000/T_0$, the slopes of the resulting lines correspond to the values of energy from Ozawa's equation (4). All model results obtained from figures 4 and 5 are presented in table 3.

*Table 3 The activation energies of crystallization determined from Kissinger and Ozawa models.*

| Method | energy | 0.5 | 1.0 | 1.5 |
|---|---|---|---|---|
| Kissinger | $E_1$(eV) | 1.75 | 1.79 | 1.73 |
| Kissinger | $E_2$(eV) | 2.70 | 2.80 | 2.72 |
| Ozawa | $E_1$(eV) | 1.97 | 1.84 | 1.83 |
| *Ozawa* | $E_2$(eV) | 2.74 | 2.69 | 2.82 |

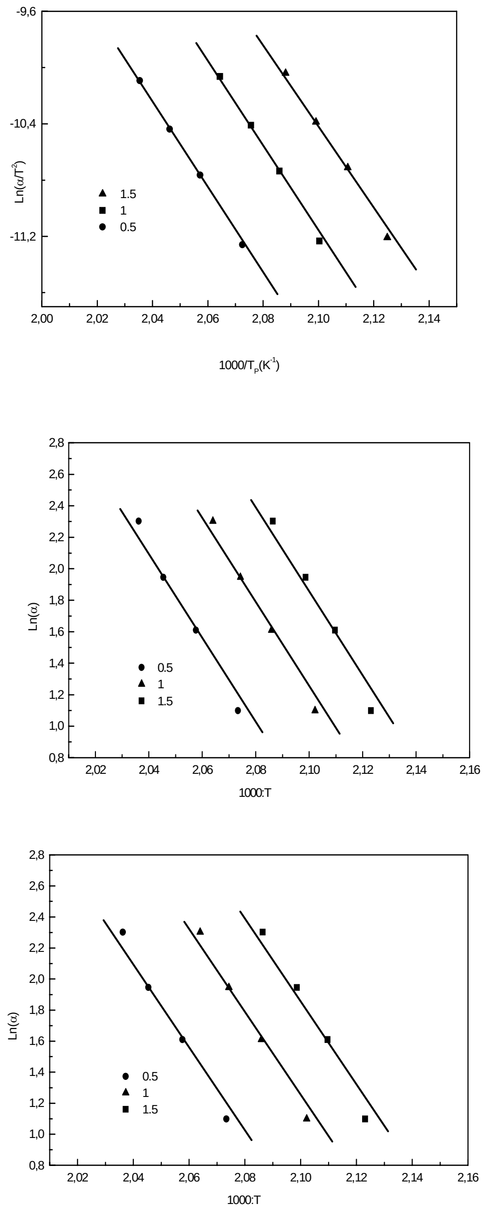

*Fig. 5. The plots of Ln(α) versus 1000/$T_0$.*

## 5. Conclusions

A study of non-isothermal crystallization for $Ge_{15.5-x}Te_{84.5}Sb_x$ (0.5 <x< 1.5) by differential scanning calorimetry (DSC) show two glass transition temperatures followed by two crystallization peaks and melting point at 385°C.

The crystallization was followed in the frame of Kissinger and Ozawa models. The activation energies of crystallization have been determined. The results are in close agreement.

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