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CRYSTALLIZATION PHENOMENA IN $GE_{15.5-X}TE_{84.5}SB_X$ (0.5 <X< 1.5) ALLOYS

L. Heireche, M. Belhadji

Département de physique, Faculté des Sciences, Université ES-Senia Oran, Algérie

The crystallization of the compositions $Ge_{15.5-x}Te_{84.5}Sb_x$ (0.5 <x< 1.5) has been investigated by differential scanning calorimetry (DSC). There were observed two crystallization peaks. The melting point was found at 385°C. The phase separation in the crystallization process corresponds to the precipitation of tellurium in its hexagonal form. The activation energies of tellurium and GeTe have been determined under dynamic condition using Kissinger's model: 1.80 eV and 2.7 eV, respectively. The validity of Kissinger's model was ascertained by comparison with the results obtained by the application of the models of Ozawa and Matusita.

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Keywords: Ge-Te-Sb, Phase change memory alloy, Amorphous, Crystallization

1. Introduction

Chalcogenide glasses of GeTeSb have been widely employed in the technology used change optical memory or compact disks and OUM (Ovonic Unified Memory). The problem of phase change in the typical Ge-Te-Sb material for memory applications is still challenging.

The composition of many telluride crystals can be changed in very broad range without any phase separation even in conditions close to thermodynamic equilibrium. Solid solutions and/or phaseswith a high density of different defects (vacancies, substitutional, interstitials) can appear even in equilibrium conditions. The structures of degenerate Ge-Sb-Te semiconductors are similar to those of intermediate compounds and metallic alloys [1,2], where broad composition regions of individual phases are easily formed without any phase separation. Such behaviour can explain the extremely rapid crystalliation without long-distance transport of the atomsor atokm groupings that should lower the crystallization speed. This idea is supported by the fact that the composition orf many phase change materials can be changed in a relatively broad range without any abrupt change of the properties: T_g, T_{cryst}, T_m. The properties of $Ge_2Sb_2Te_5$, $GeSb_2Te_4$ and $GeSb_4Te_7$ are very similar, their phase diagrams and melting temperatures are, also, similar [3, 4]. It is possible to prepare their alloys in a broad range of composition, from $SbTe_3$ to Sb_4Te. As the difference in the physical properties of $Ge_2Sb_2Te_5$, $GeSb_2Te_4$ and $GeSb_4Te_7$ [4] is not large, solid solutions can be formed without abrupt changes of the properties. The formation of the solid solutions means in fact the formation of substitutional defects, as shown by Yamada [5, 6] and Frumar [7]. The alloys and melts of Ge, Sb, Te can crystallize very easily due to possible substitution of atoms, without necessary formation of several phases during the crystallizastion of the non-stoichiometric melts. The differences in the structure of $Ge_2Sb_2Te_5$, $GeSb_2Te_4$ and $GeSb_4Te_7$ [6, 8] is only in numer and ordering of the stacking layers of Sb, Te and Ge, and stacking defects can be probably also formed by non-equilibrium crystallization.

In this paper there are reported the results obtained by differential scanning calorimetry (DSC) on the crystallization processes occurring in these glasses in a narrow composition range: $Ge_{15.5}Te_{84.5}Sb_x$ (0.5 <x< 1.5).

2. The study of the crystallization zone

The analysis of the differential enthalpy is very useful in the investigation of the reactions that take place during the heating (or cooling) of the materials with a constant rate of heating (cooling), i.e. in dynamic regime.

The thermograms obtained by DSC for various heating Rates allowed for getting a full kinetics for the determination of the crystallization, as e.g. the Avrami index, the activation energy. We succeeded to put in evidence the influence of antimony on the crystallization. In the Figs. (1-3) are shown the thermograms obtained for three samples with different heating rates, α. These thermograms exhibit two crystallization peaks, as opposite to the eutectic composition, which exhibits only one peak (Fig. 4).

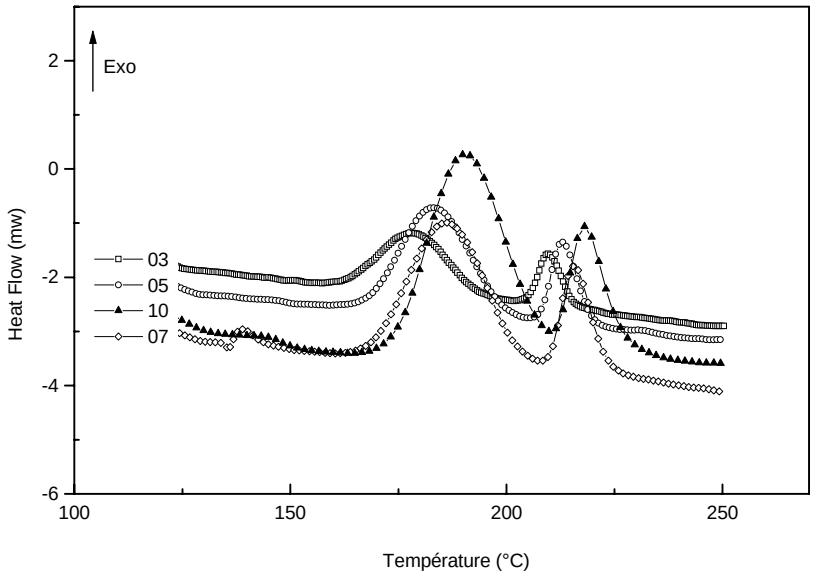

Fig. 1. The thermogram of the alloy $Ge_{15}Te_{84.5}Sb_{0.5}$ for various heating rates.

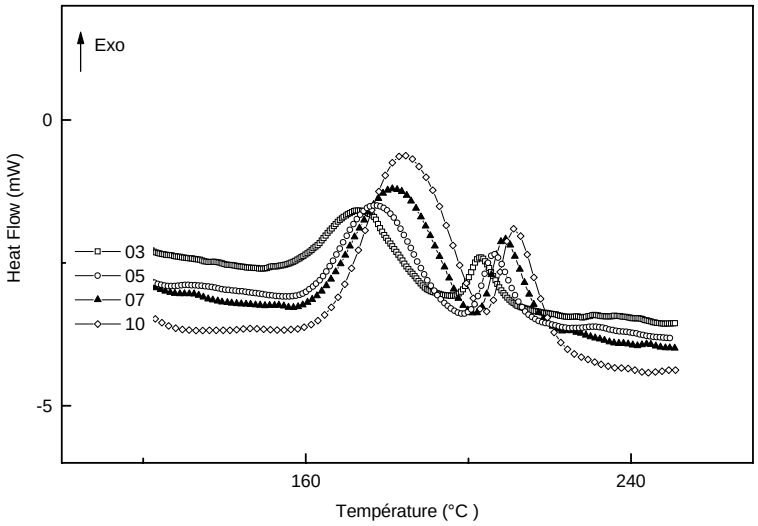

Fig. 2. The thermogram of the alloy $Ge_{14.5}Te_{84.5}Sb_{01}$ for various heating rates.

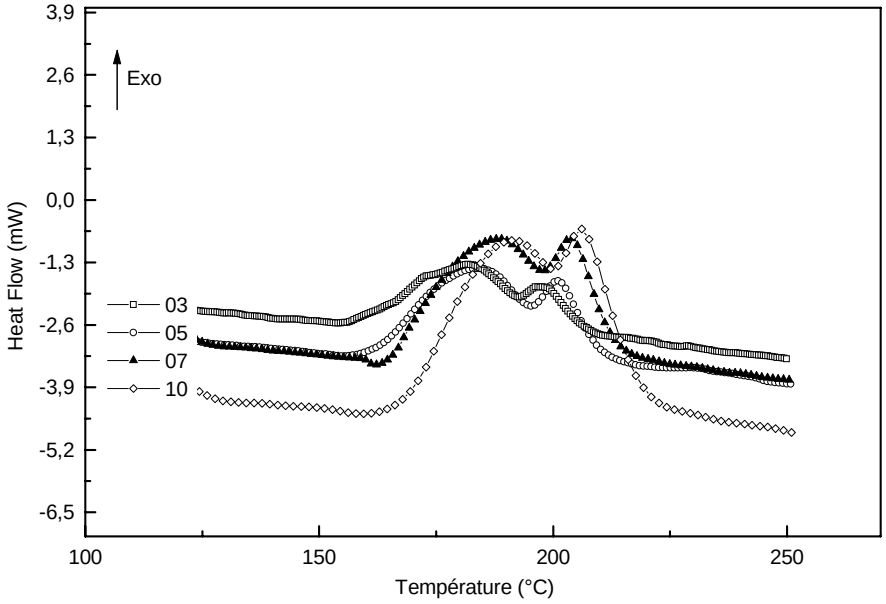

Fig. 3. The thermogram of the alloy $Ge_{14}Te_{84.5}Sb_{1.5}$ for various heating rates.

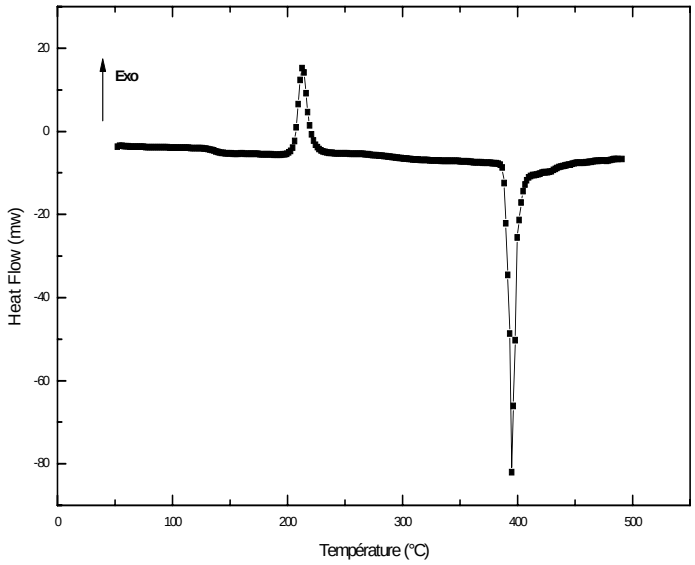

Fig. 4. The thermogram of the alloy $Ge_{15}Te_{82}Sb_3$ for the heating rate of 10 °C/min.

The plots show the evolution of the crystallization peaks as a function of the heating rate, α. It is remarkable that the two crystallization peaks shift towards high temperatures when the heating rate increases.

It is also remarkable that the two peaks of $Ge_{15}Te_{84.5}Sb_{0.5}$ are distinctly separated.The increase of the antimony content in the alloy gives rise to the approaching of the peaks in $Ge_{15}Te_{84.5}Sb_1$, and a partial superposition in $Ge_{15}Te_{84.5}Sb_{1.5}$ (Fig. 5), T_{c1} et T_{c2} increases with the Sb content (Fig. 6).

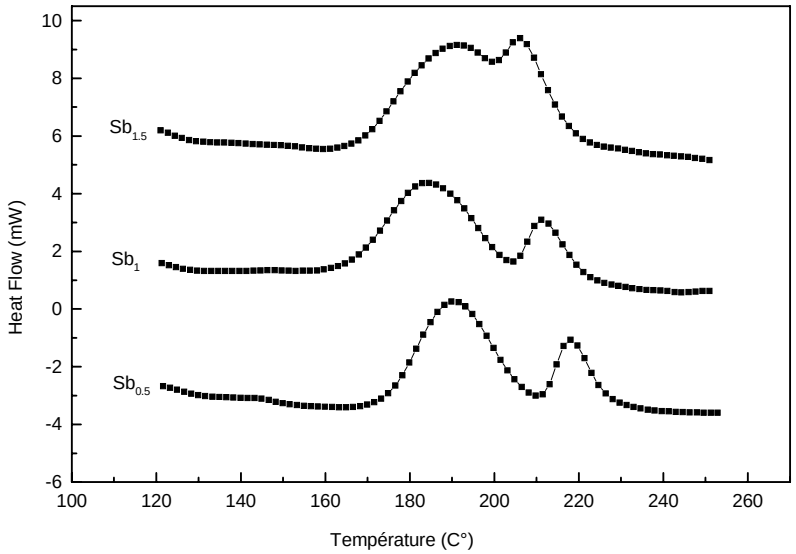

Fig. 5. The thermograms of the alloy $Ge_{15.5-x}Te_{84.5}Sb_x$ (x=0.5 ,1 , 1.5) at the rate of 10 °C/min.

Table 1. The thermal parameters of the alloys in the system Ge-Sb-Te for a heating rate of 10 °C/min.

X	0.5	1	1.5	References
T_{c1} (°C)	174	166	168	Our results
T_{c2} (°C)	210	203	199	
Hc_1(J/g)	29.451	39.949	38.697	
Hc_2 (J/g)	19.489	13.204	13.292	
T_{c1} (°C)	174	166	168	[1]
T_{c2} (°C)	212	206	200	

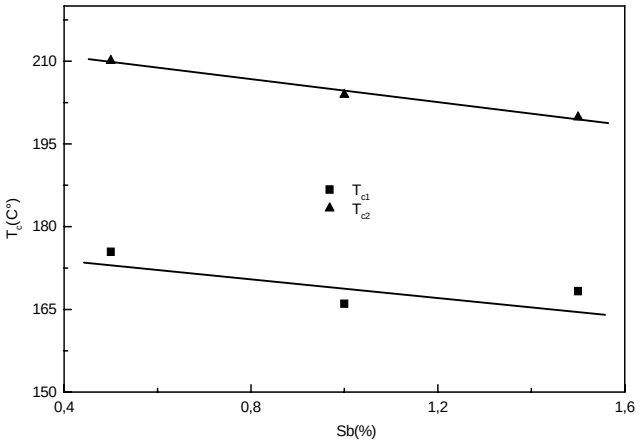

Fig. 6. The variation of T_c as a function of antimony content.

3. Determination of the crystallization parameters

The determination of the crystallization parametersof the investigated materials, as e.g. the activation energy of the crystallization process and, E_a, and the Avrami index n, is performed in dynamic regime. For this we have applied the Matusita model developed for oxide glasses. In the same time we tried to make an analogy with the models of Kissinger and Ozawa.

3.1. The investigation of the crystalline fraction

In general, the studies orf the crystallizastion parameters are carried out on only one crystallization peak, that is related to one vitreous phase. The crystallized fraction is determined by the Borchard method. For every value of the crystallized fraction, x, corresponds a time duration, t, and a well-defined temperature T.

$$x(t) = S/S_0 \qquad (1)$$

where S is the area of the peak considered from the moment t_1 that denotes the start of the crystallization process and a moment « t » for which it is deduced the value of the crystallized fraction. S_0 is the area under the peak formed at the end of the crystallization at the moment t_2.

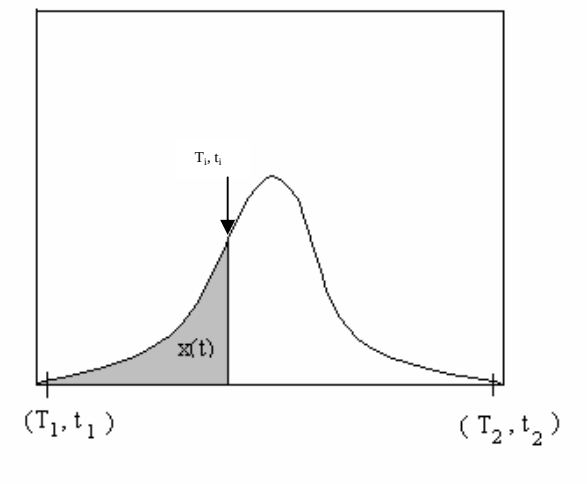

Fig. 7 The application of the Bochard method.

In order to understand the special phenomenon related to the two crystallization peaks firstly one studies the evolution of of the crystalline fraction, x, with the time.

For this purpose the fraction x has been calculated by both methods. The first method consists in the study of the system as a function of the total crystalline fraction with the relation (1)

$X = \frac{S_X}{S_0}$ $x \in [T_i, T_F]$.

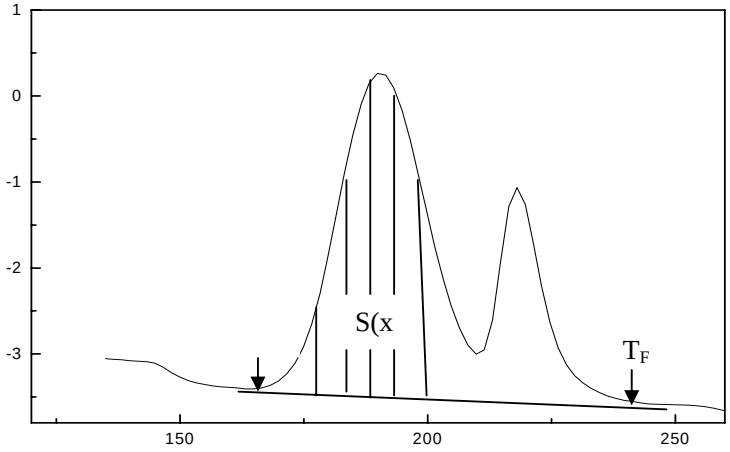

Fig. 8 The determination of the crystalline fraction.

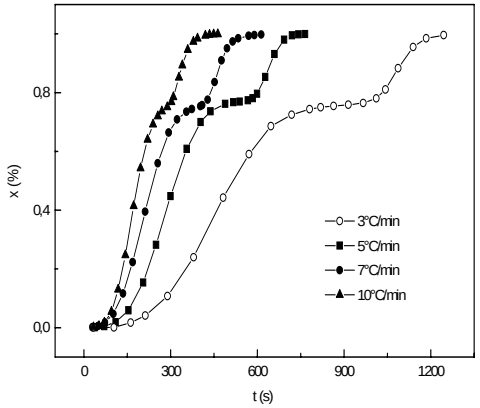

Fig. 9. Evolution of the crystalline fraction as a function of time for $Ge_{14.5}Te_{84.5}Sb_{0.5}$.

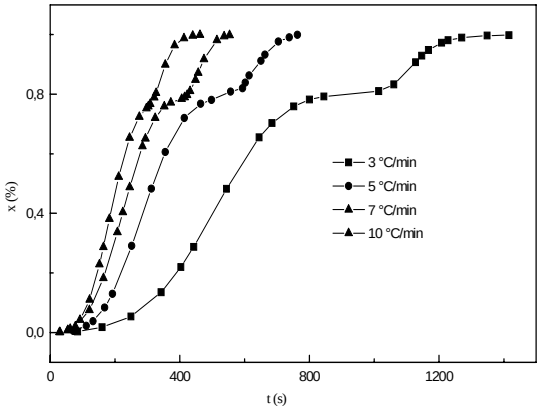

Fig. 10 The evolution of the crystalline fraction as a function of time for $Ge_{15}Te_{84.5}Sb_1$.

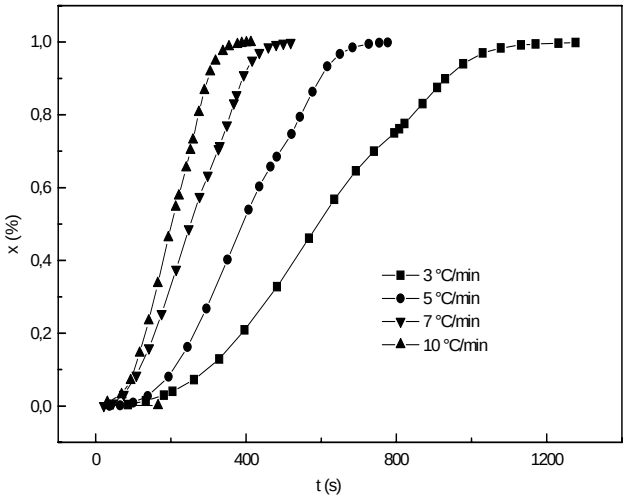

Fig. 11. The evolution of the crystalline fraction as a function of time for $Ge_{14.5}Te_{84.5}Sb_{1.5}$.

In the second method it is investigated the crystalline fraction for every peak as an unique system with: $X_1=\frac{S_X}{S_1}$ for x $[T_i, T_{c2}]$

$$X_2=\frac{S_X}{S_2} \quad S_X = S_3 - S_1 \quad \text{avec } x \in [T_{c2}, T_F] \tag{2}$$

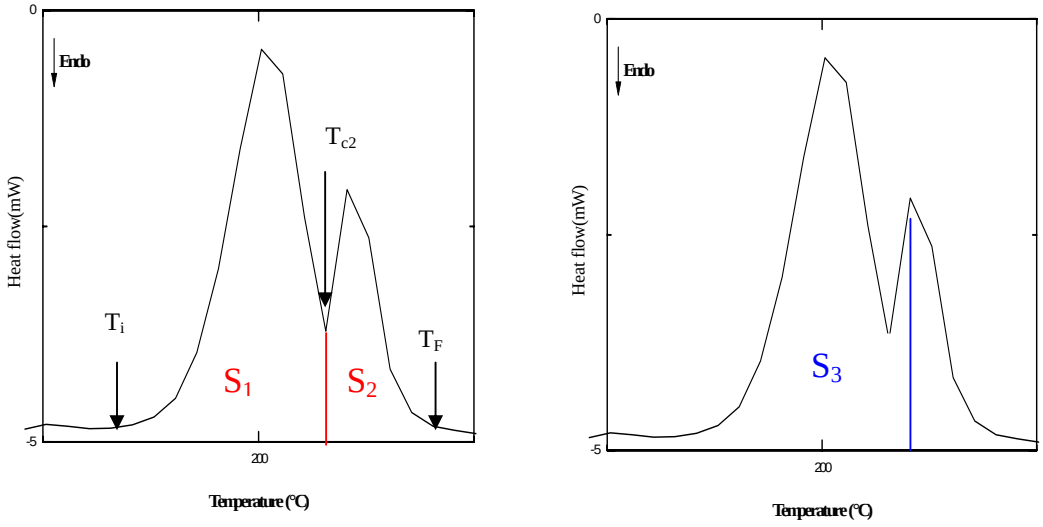

Fig. 12. The determination of the crystalline fraction.

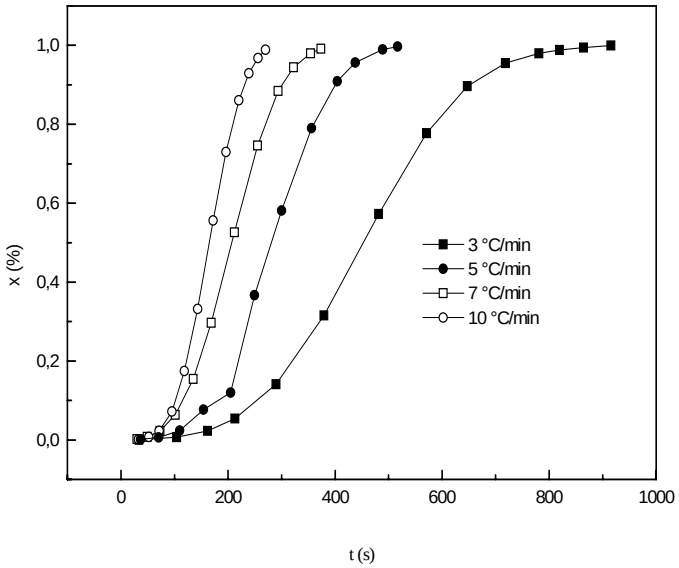

Fig. 13. The evolution of the crystalline fraction obtained from the first peak for $Ge_{15.5}Te_{84.5}Sb_{0.5}$.

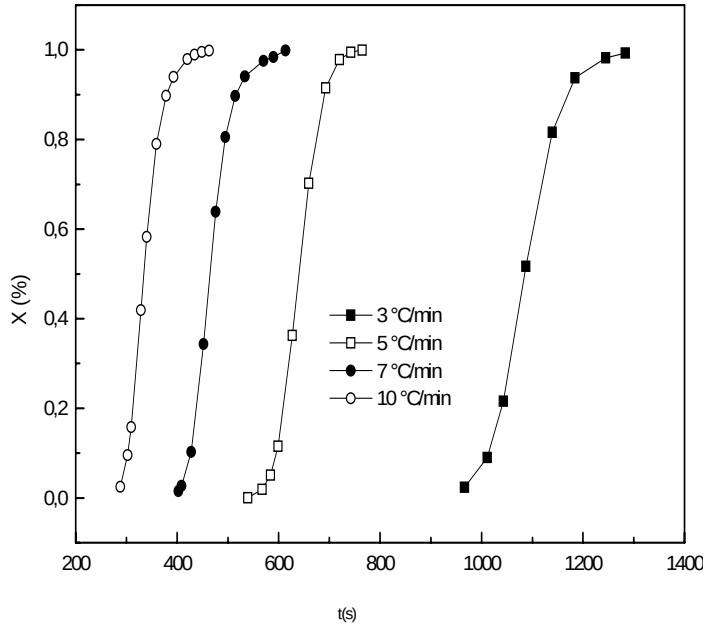

Fig. 14. The evolution of the crystalline fraction obtained from the second crystallization peak for $Ge_{15.5}Te_{84.5}Sb_{0.5}$.

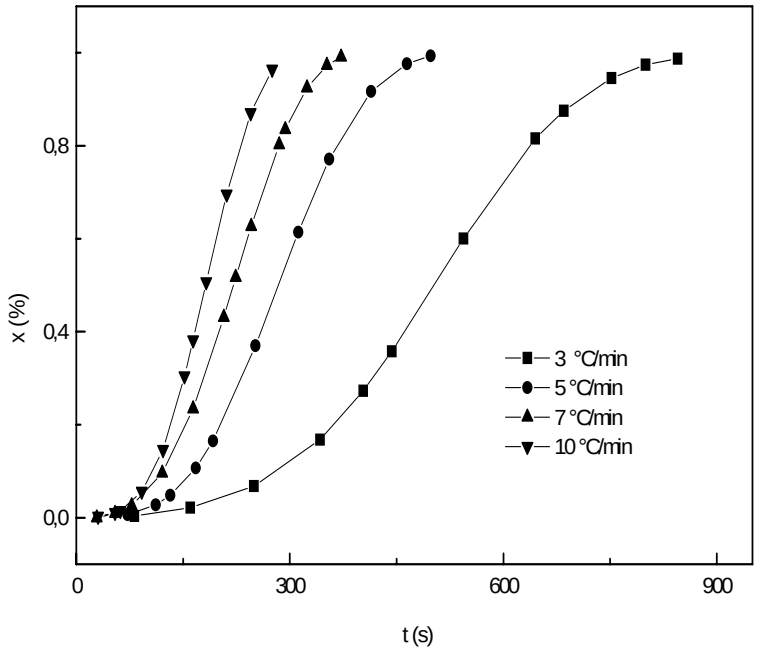

Fig. 15. The evolution of the crystalline fraction obtained from the second crystallization peak for $Ge_{15}Te_{84.5}Sb_{1.}$

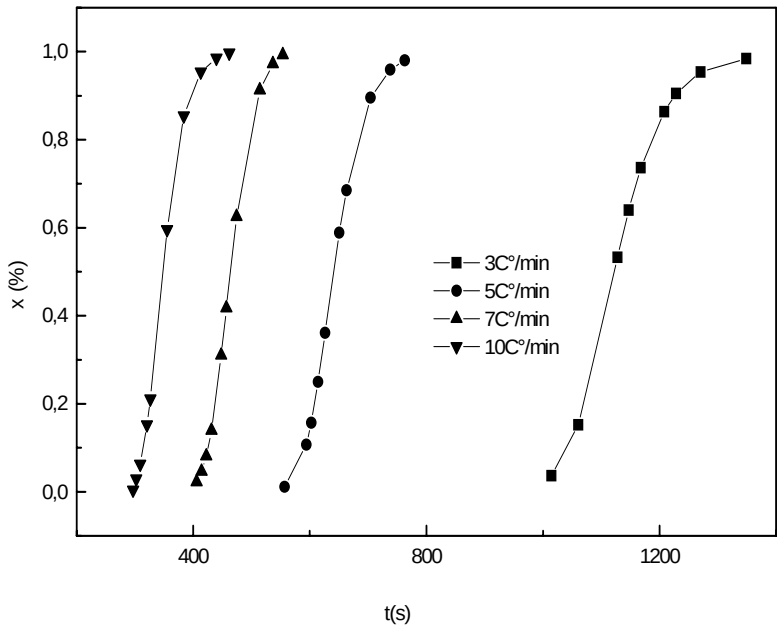

Fig. 16. The evolution of the crystalline fraction obtained from the second crystallization peak for $Ge_{15}Te_{84.5}Sb_{1.}$

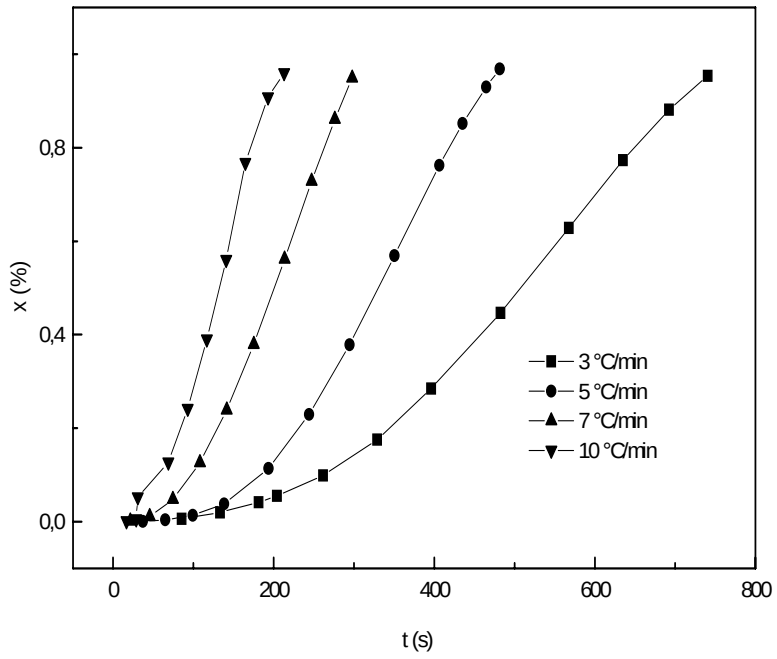

Fig. 17. The evolution of the crystalline fraction obtained from the second crystallization peak for $Ge_{14.5}Te_{84.5}Sb_{1.5}$

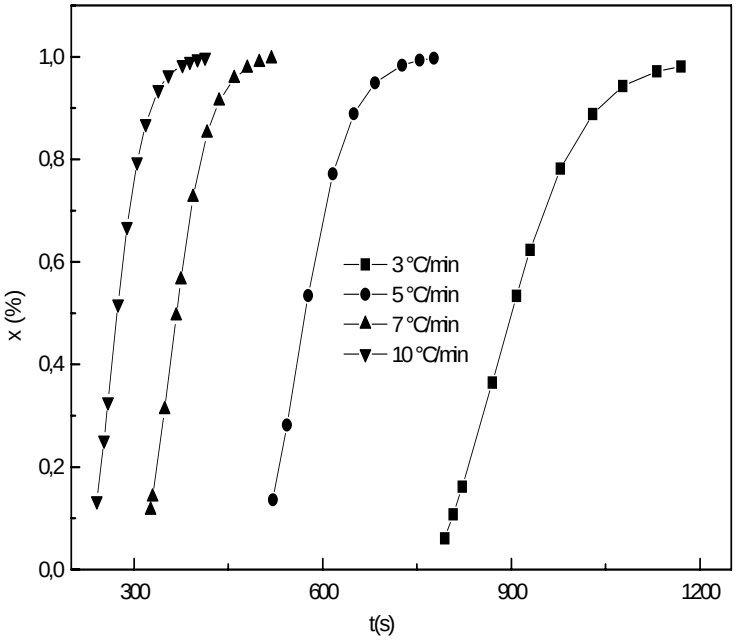

Fig. 18. The evolution of the crystalline fraction obtained from the second crystallization peak for $Ge_{14.5}Te_{84.5}Sb_{1.5.}$

After drawing the curves of the crystalline fraction rfor the three samples with the two methods, one remarks that the system behavs as a material that shows phase separation, because the crystalline phase in the first method is described by two exponentials separated by some time interval. This time interval decreases when the antimony content is enhanced, or when the heating rate is increased. The crystallization time decreases with the increase of the heating rate.

We have used the second method for the calculation of the crystallization parameters. The hypothesis of Ozawa for the maximum of the peak corresponding to the fraction x= 0.63 is applicable in this method (Table 2, 3).

Table 2. The values of T_p and $T_{M0.63}$ for the first crystallization peak (in °C).

Composition	$Ge_{15}Sb_{0.5}Te_{84.5}$	$Ge_{14.5}Sb_1Te_{84.5}$	$Ge_{14.5}Sb_{1.5}Te_{84.5}$
T_p	190	184	191
$T_{M0.63}$	193	188	191

Table 3. The values of T_p and $T_{M0.63}$ for the second crystallization peak (in °C).

Composition	$Ge_{15}Sb_{0.5}Te_{84.5}$	$Ge_{14.5}Sb_1Te_{84.5}$	$Ge_{14.5}Sb_{1.5}Te_{84.5}$
T_p	218	211	206
$T_{M0.63}$	220	214	209

4. Conclusions

From the thermal study of the Ge-Sb-Te compositions in the non-crystalline phases there was possible to deduce the softening tempearature and crystallization temperature. In both cases double peaks of softeneing and crystallization are evidenced. Therefore, one concludes that the initial compositions, either are already phase separated in the amorphous phase or give rise to phase separation during the heating process.

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