Thermal Stability and Tg Characteristics of GeTeSb Glasses

Abdelhamid Badaoui[1*] and Maamar Belhadji[1,2]

[1]*Laboratoire de Chimie des Polymeres, LCP, Es-Senia University, Oran, 31000, Algeria.*
[2]*Physics Department, Es-Senia University, Oran, 31000, Algeria.*

Authors' contributions

This work was carried out in collaboration between all authors. Author AB designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Author MB managed the analyses of the study and the literature searches and correction after review. All authors read and approved the final manuscript.

Research Article

ABSTRACT

Important physical properties, such as coordination number and mean bond energy of Te based chalcogenide system (GeTeSb) are studied for different Te contents, each one with different compositions when replacing Ge atoms with Sb ones. We found that these properties decrease with increasing Sb contents, and hence with decrease of average coordination number. The thermal stability of the system is evaluated according to Dietzel criterion ΔT. The glass transition temperature T_g is then deduced with a suitable proportionality with the mean bond energy and compared to experiment values. This glass temperature is also found to be related with linear function to the average coordination number according to Gibbs-DiMarzio modified equation and the parameters T_0 and β are determined.

Keywords: DSC; chalcogenide glasses; GeTeSb; coordination number; average bond energy; glass transition temperature.

Corresponding author: Email: aeh_badaoui@yahoo.fr;

1. INTRODUCTION

Chalcogenide glasses have become with great interest and widely studied by many authors as they show electrical and optical properties making them useful for several potential applications in view of fabrication of various solid state devices [1,2]. They exhibit threshold and memory switching behaviour as well as infrared transmission. They have been also applied in xerography [3], photolithography [4] and in the fabrication of inexpensive solar cells [5]. New applications of amorphous materials such as image sensors, thermoelectric properties and optical recording [6] have become realisable due to recent progress in preparation techniques. The properties of chalcogenide materials such optical, electrical and physical properties can be controlled by changing their chemical composition [7]. When doped with metal impurities, these materials become multipurpose by the modification of their properties [8]. Multicomponent glasses are more attracting as they are more useful for many of these applications [9,10]. The binary GeTe alloys are phase change ovonic materials and exhibit switching properties [11]. The ternary system GeTeSb has been highly used in phase change memories.

In this paper, some physical properties such as coordination number, mean bond energy and thermal stability are investigated for GeTeSb system alloys with different Te contents, each one with different compositions. The effect of antimony addition is discussed, a theoretical deduction of the glass transition temperature is proposed and the values are compared to experimental results.

2. EXPERIMENTAL DETAILS

The preparation of alloys was in two steps. First the three elements (99.999 % purity) were weighted in suitable quantities and introduced in a quartz ampoule and sealed in vacuum of 10^{-5} Pa. Then, the ampoules were placed in a horizontally rotating oven and annealed at 1000ºC for 3 hours. Finally, the ampoules were quenched into ice-cold water to avoid crystallization. After breaking the quartz ampoules, amorphous nature of these alloys were verified by X-Ray diffraction (XRD) technique. The XRD spectra (not shown) do not contain any prominent peak, which confirms the amorphous nature of the samples.

3. RESULTS AND DISCUSSION

Fig. 1 shows the DSC thermogram for $Ge_{14.5}Te_{84.5}Sb_1$ glassy alloy under non-isothermal condition as an example. The presence of two T_g and two T_c peaks is evident (same remark for all 84.5% at Te) and points to a phase separation in the glassy system. For the other compositions of Te there is a single glassy phase (not shown). The characteristic temperatures are listed in Table 1.
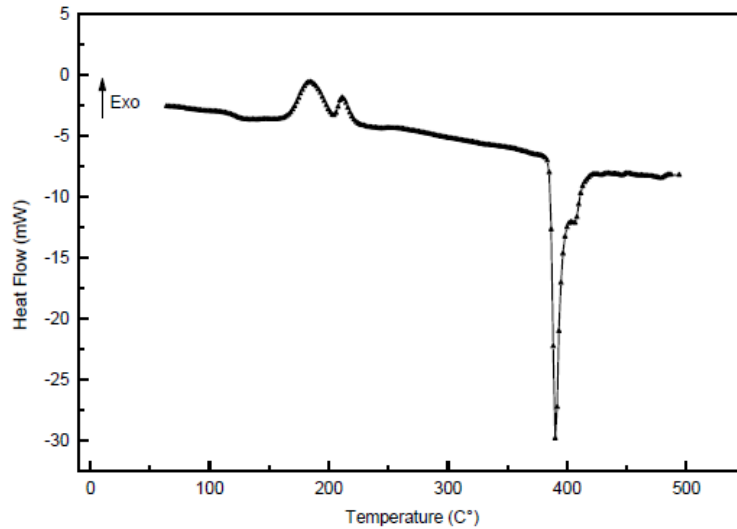
Fig. 1. Differential thermal analysis of $Ge_{14.5}Te_{84.5}Sb_1$ at rate of 10⁰C

The average coordination number is evaluated according to the standard procedure requiring the knowledge of the coordination of all the elements of the glassy alloy [12,13]. For the considered system GexTeySbz, it is given by:

$$n = \frac{xN_{Ge} + yN_{Te} + zN_{Sb}}{x + y + z} \tag{1}$$

where x, y and z are atomic fractions of Ge, Te and Sb respectively and $N_{Ge} = 4$, $N_{Te} = 2$ and $N_{Sb} = 3$ are their respective coordination numbers. The calculated values of the average coordination number are given in Table 1.

Table 1. Glass compositions, average coordination number, measured glass transition and crystallization temperatures, Dietzel temperature interval, mean bond energy and theoretical glass transition temperature

Composition	n	T_{gexp} (K)	T_c (K)	ΔT (K)	<E> (KJ/mol)	<E> (eV)	T_{gtheo} (K)
$Ge_{20}Te_{80}$	2.40	420	488	68	164.82	1.710	416.7
$Ge_{17}Te_{80}Sb_3$	2.37	404	479	75	161.21	1.673	405.2
$Ge_{15}Te_{80}Sb_5$	2.35	393	455	62	158.83	1.648	397.5
$Ge_{18}Te_{82}$	2.36	-	-	-	160.72	1.668	403.7
$Ge_{17}Te_{82}Sb_1$	2.35	400	473	73	159.56	1.656	399.9
$Ge_{16}Te_{82}Sb_2$	2.34	396	470	74	158.40	1.644	396.2
$Ge_{15}Te_{82}Sb_3$	2.33	392	458	66	157.45	1.634	393.1
$Ge_{14}Te_{82}Sb_4$	2.32	388	447	59	156.26	1.622	389.4
$Ge_{13}Te_{82}Sb_5$	2.31	386	438	52	154.98	1.608	385.0
$Ge_{16}Te_{84}$	2.32	-	-	-	156.90	1.628	391.2
$Ge_{15}Te_{84.5}Sb_{0.5}$	2.305	393	447	54	155.44	1.613	386.6
$Ge_{14}Te_{84.5}Sb_{1.5}$	2.295	387	441	54	154.34	1.602	383.2
$Ge_{13}Te_{84.5}Sb_{2.5}$	2.285	381	433	52	153.25	1.590	379.4

It is seen, from Table 1, that the average coordination number values decrease for each Te composition, with increasing Sb content. This behavior is caused by the substitution of Ge atoms (from group IV) with Sb ones (from group V).

From the characteristic temperatures, we estimated the thermal stability of the system using Dietzel criterion $\Delta T = T_c - T_g$ [14]. According to this criterion, the kinetic resistance to crystallization increases with increasing ΔT. According to this criterion, the kinetic resistance to crystallization increases with increasing ΔT. This value gives an indication of the thermal stability of the glassy system, a small value of ΔT means that the glass contains structural units with high crystallization tendency and vice versa. From Table 1 and Fig. 2, we can see that glass alloy compositions Ge17Te80Sb3 gives the most stable glass with the maximum value of ΔT. The presence of maximum in ΔT values can be understood on the basis of Phillips-Thorpe [12,15-18] constraint theory for glasses with covalent bonds. According to this theory, for alloy compositions having high glass forming ability and where only short range order structures are considered, the number of degrees of freedom, N_d in a covalently bonded glass exhausts the number of constraints, $N_{c\alpha}$ due to bond stretching, and bond bending $N_{c\beta}$, with $N_c = N_{c\alpha} + N_{c\beta}$. The condition $N_c = N_d$, leaded Philips to conclude that the stability of the network having the critical coordination number n = 2.4 is optimised. Thorpe [16] found the same result by counting the number of zero-frequency modes. He showed that undercoordinated networks would possess a finite fraction of zero-frequency modes in the absence of the weaker longer range forces. The number of zero-frequency mode per atom is given by:

$$f = 2 - \frac{5}{6} n \qquad (2)$$

This number approaches zero as n approaches the critical value of 2.4, where there is a phase transition from underconstraints floppy network to overconstrainted rigid network having maximum stability. We consider then that the Phillips'-Thorpe threshold is realized for the investigated system.
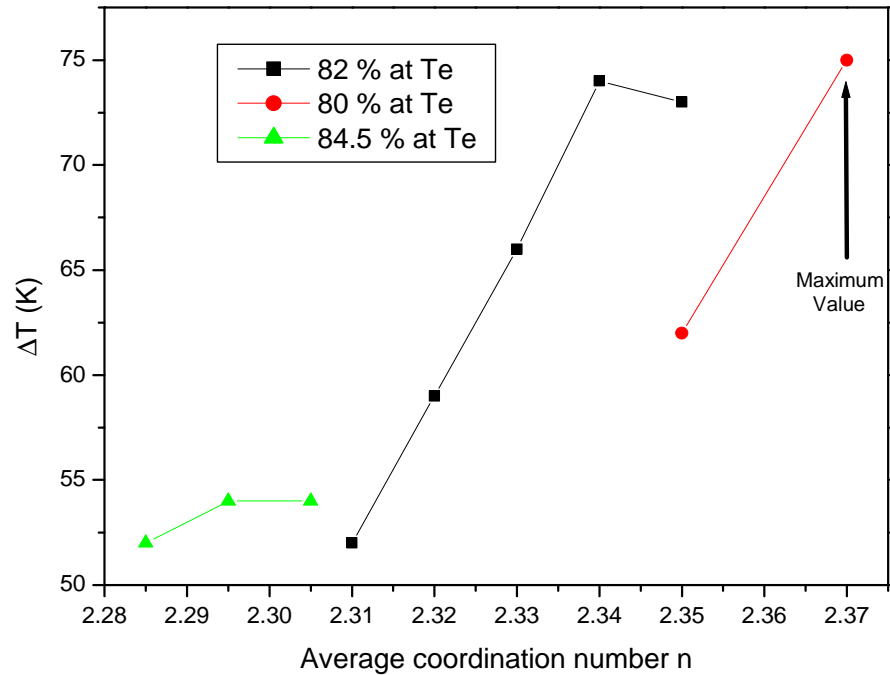
Fig. 2. Dietzel temperature interval versus average coordination number for the different ternary compositions

In the other hand, a linear correlation between the glass transition temperature and the overall mean bond energy $\langle E \rangle$ of the glassy network is observed for many chalcogenide systems. The mean bond energy is calculated using the covalent bond approach (CBA) [19], which is given by:

$$\langle E \rangle = E_{cl} + E_{rm} \tag{3}$$

where E_{cl} is the overall contribution towards bond energy arising from strong bonds, and E_{rm} is the contribution arising from weaker bonds that remain after the number of strong bonds becomes maximum.

For the investigated system $Ge_x Te_y Sb_z$:

$$E_{cl} = 4x D_{Ge-Te} + 3z D_{Sb-Te} \tag{4}$$

where 4, x, 3 and z correspond to the coordination number and atomic concentration of Ge and Sb atoms respectively. The heteronuclear bond energy is calculated using the relation given by Pauling [20]:

$$D_{A-B} = \left(D_{A-A} \times D_{B-B} \right)^{0.5} + 30 \left(\chi_A - \chi_B \right)^2 \tag{5}$$

where, χ_A, χ_B, D_{A-A} and D_{B-B} are respectively the electronegativity and the homonuclear bond energies of A and B atoms. The average bond energy per atom of the remaining matrix is given by:

$$E_{rm} = \left(1 - \frac{4x - 3z}{2}n\right)D_{Te-Te} \qquad (6)$$

The calculated values of the mean bond energy $\langle E \rangle$ are listed in Table 1. It's understood that $\langle E \rangle$ is influenced by the degree of cross-linking, the bond energy, the average coordination number and the bond type, and all these factors influence the glass transition temperature of the glassy system.

The later, is considered as one of the most important parameters used for characterizing a glassy state and can be theoretically calculated using different methods [21]. For many chalcogenide systems, this glass transition temperature Tg is found to be proportional to the mean bond energy value of the covalent glassy network [19,22-24]. For our system, we proposed a theoretical deduction to estimate this parameter in units of eV:

$$T_{gtheo} = 311\left(\langle E \rangle - 0.37\right) \qquad (7)$$

From Fig. 3, it's interesting to observe that the glass transition temperature depends linearly to the average coordination number when it's examined in totality for all the compositions. This observation is in accordance with the modified Gibbs-DiMarzio [25] equation:

$$T_g = \frac{T_0}{1 - \beta(n-2)} \qquad (8)$$

where T_0 is the glass transition temperature of the non-cross linked initial chain, β a system parameter and n the average coordination number. Eq. (9) can be expressed for high chalcogene limit as:

$$T_g \cong T_0\left[1 + \beta(n-2)\right] \qquad (9)$$

From the linear fit of the plot of T_g versus n (Fig. 3), we deduced the parameters of Eq. (9): $T_0 = 288.8\,K$; $\beta = 1.096$
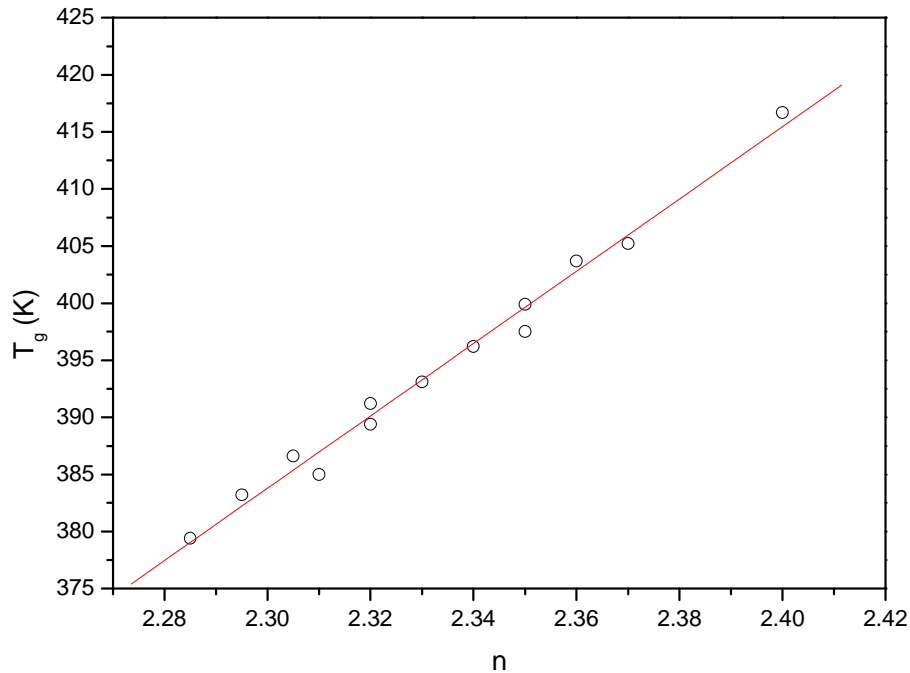
Fig. 3. Glass transition temperature versus average coordination number for GeTeSb

In Table 1, are also listed and compared, the experimental and the theoretical values of the glass transition temperature (T_{gexp} and T_{gtheo}) and it is seen that the values are in good agreement, it is also observed that the calculated values of $\langle E \rangle$, and hence the values of T_g (experimental and theoretical) increase with increasing n. This may be explained on the fact that Sb makes stronger bonds with Ge and weaker bonds with Te, indicating a cross linking of the Ge-Te chains with Sb.

4. CONCLUSION

Thermal stability of the glassy system GeTeSb has been studied with different compositions using the characteristic temperatures, and the results showed a high stability according to Dietzel temperature interval when the average coordination number approaches the critical value of n = 2.4, realizing the Phillips'-Thorpe percolation threshold. The mean bond energy is calculated using the covalent bond approach and the glass transition temperature was deduced theoretically using a suitable relation and compared to experiment. This glass transition temperature is found to be depending linearly to the mean bond energy as for many other glassy systems. Both mean bond energy and glass transition temperature are found to be in decrease with increase of Sb contents leading to the increase in the average binding strength.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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