Thermal Stability and Tg Characteristics of GeTeSb Glasses

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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.

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 1000 °C for 3 hours. Finally, the ampoules were quenched into ice-cold water to avoid

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43 crystallization. After breaking the quartz ampoules, amorphous nature of these alloys were verified by X-Ray diffraction
44 (XRD) technique. The XRD spectra (not shown) do not contain any prominent peak, which confirms the amorphous nature
45 of the samples.
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48 **3. RESULTS AND DISCUSSION**
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50 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
51 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
52 glassy system. For the other compositions of Te there is a single glassy phase (not shown). The characteristic
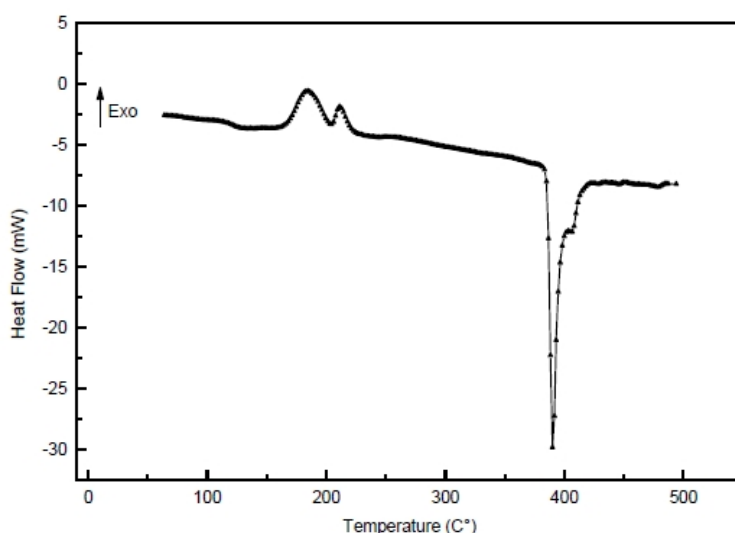53 temperatures are listed in Table 1.
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56
57 **Fig. 1. Differential thermal analysis of $Ge_{14.5}Te_{84.5}Sb_1$ at rate of 10 °C**

58
59 The average coordination number is evaluated according to the standard procedure requiring the knowledge of the
60 coordination of all the elements of the glassy alloy [12,13]. For the considered system GexTeySbz, it is given by:
61

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

63
64 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
65 coordination numbers. The calculated values of the average coordination number are given in Table 1.
66
67 **Table 1.   Glass compositions, average coordination number, measured glass transition and crystallization**
68 **temperatures, Dietzel temperature interval, mean bond energy and theoretical glass transition temperature.**
69

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

70

71 From the characteristic temperatures, we estimated the thermal stability of the system using Dietzel criterion $\Delta T = T_c - T_g$

72 [14]. According to this criterion, the kinetic resistance to crystallization increases with increasing ΔT. This value gives an

73 indication of the thermal stability of the glassy system, a small value of ΔT means that the glass contains structural units

74 with high crystallization tendency and vice versa. From Table 1 and Fig. 2, we can see that glass alloy compositions

75 Ge17Te80Sb3 gives the most stable glass with the maximum value of ΔT. The presence of maximum in ΔT values can

76 be understood on the basis of Phillips-Thorpe [12,15-18] constraint theory for glasses with covalent bonds. According to

77 this theory, for alloy compositions having high glass forming ability and where only short range order structures are

78 considered, the number of degrees of freedom, N_d in a covalently bonded glass exhausts the number of constraints,

79 $N_{c\alpha}$ 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

80 conclude that the stability of the network having the critical coordination number n = 2.4 is optimised. Thorpe [16] found

81 the same result by counting the number of zero-frequency modes. He showed that undercoordinated networks would

82 possess a finite fraction of zero-frequency modes in the absence of the weaker longer range forces. The number of zero-

83 frequency mode per atom is given by:

84

85 $$f = 2 - \frac{5}{6}n \qquad\qquad (2)$$

86
87
88 This number approaches zero as n approaches the critical value of 2.4, where there is a phase transition from

89 underconstraints floppy network to overconstrainted rigid network having maximum stability. We consider then that the

90 Phillips'-Thorpe threshold is realized for the investigated system.
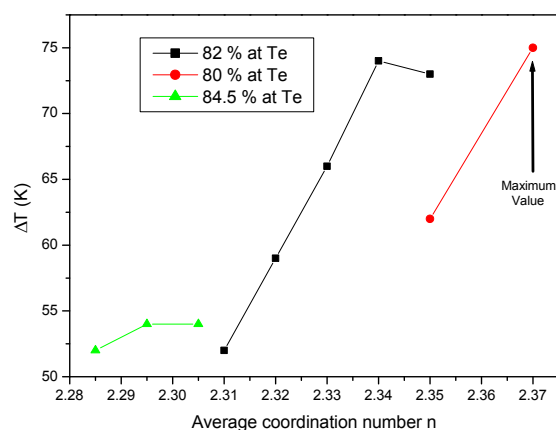
91
92 **Fig. 2. Dietzel temperature interval versus average coordination number for the different ternary compositions**
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94 In the other hand, a linear correlation between the glass transition temperature and the overall mean bond energy $\langle E \rangle$ of

95 the glassy network is observed for many chalcogenide systems. The mean bond energy is calculated using the covalent

96 bond approach (CBA) [19], which is given by:

97

98 $$\langle E \rangle = E_{cl} + E_{rm} \qquad\qquad (3)$$

99

100 where E_{cl} is the overall contribution towards bond energy arising from strong bonds, and E_{rm} is the contribution arising

101 from weaker bonds that remain after the number of strong bonds becomes maximum.

102 For the investigated system $Ge_xTe_ySb_z$:

103

104 $$E_{cl} = 4xD_{Ge-Te} + 3zD_{Sb-Te} \qquad (4)$$

105

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

108

109 $$D_{A-B} = \left(D_{A-A} \times D_{B-B}\right)^{0.5} + 30\left(\chi_A - \chi_B\right)^2 \qquad (5)$$

110

111 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
112 atoms. The average bond energy per atom of the remaining matrix is given by:

113

114 $$E_{rm} = \left(1 - \frac{4x - 3z}{2} n\right) D_{Te-Te} \qquad (6)$$

115
116

117 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
118 degree of cross-linking, the bond energy, the average coordination number and the bond type, and all these factors
119 influence the glass transition temperature of the glassy system.
120 The later, is considered as one of the most important parameters used for characterizing a glassy state and can be
121 theoretically calculated using different methods [21]. For many chalcogenide systems, this glass transition temperature Tg
122 is found to be proportional to the mean bond energy value of the covalent glassy network [19, 22-24]. For our system, we
123 proposed a theoretical deduction to estimate this parameter in units of eV:

124

125 $$T_{gtheo} = 311\left(\langle E \rangle - 0.37\right) \qquad (7)$$

126

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

130

131 $$T_g = \frac{T_0}{1 - \beta(n-2)} \qquad (8)$$

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

134

135 $$T_g \cong T_0\left[1 + \beta(n-2)\right] \qquad (9)$$

136

137 From the linear fit of the plot of T_g versus n (Fig. 3), we deduced the parameters of Eq. (9):
138 $T_0 = 288.8\,K;\ \ \beta = 1.096$

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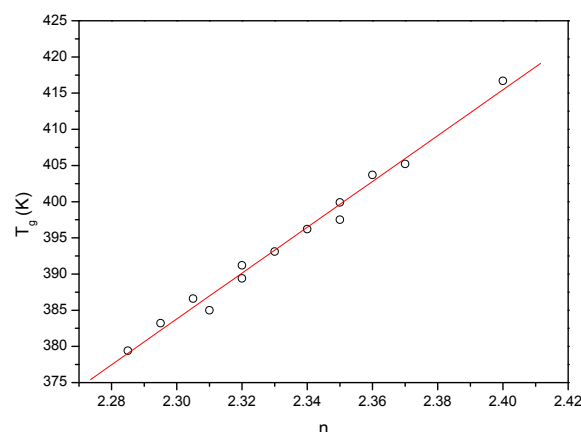
Fig. 3. Glass transition temperature versus average coordination number for GeTeSb.

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144 In Table 1, are also listed and compared, the experimental and the theoretical values of the glass transition temperature
145 (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
146 $\langle E \rangle$, and hence the values of T_g (experimental and theoretical) increase with increasing n. This may be explained on the
147 fact that Sb makes stronger bonds with Ge and weaker bonds with Te, indicating a cross linking of the Ge-Te chains with
148 Sb.
149
150 **4. CONCLUSION**
151
152 Thermal stability of the glassy system GeTeSb has been studied with different compositions using the characteristic
153 temperatures, and the results showed a high stability according to Dietzel temperature interval when the average
154 coordination number approaches the critical value of n = 2.4, realizing the Phillips'-Thorpe percolation threshold. The
155 mean bond energy is calculated using the covalent bond approach and the glass transition was deduced theoretically
156 using a suitable relation and compared to experiment. This glass transition temperature is found to be depending linearly
157 to the mean bond energy as many other glassy systems. Both mean bond energy and glass transition temperature are
158 found to be in decrease with increase of Sb contents leading to the increase in the average binding strength.
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