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ESTIMATION OF GLASS TRANSITION TEMPERATURE OF $Al_x(Ge_2Sb_2Te_5)_{1-x}$ GLASSY SYSTEM

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Phase change technology using resistance contrast is most promising candidate being investigated to replace DRAM technology in order to get increased and volatile memory capacity. The most successful material so far is $Ge_2Sb_2Te_5$. To optimize its properties we study the Aluminium modified system. The glass transition temperature of $Al_x(Ge_2Sb_2Te_5)_{1-x}$ is estimated on the basis of model presented by M. H. R Lankhorst. The said model is applicable to covalent amorphous materials of elements from group I B-VI B for which average number of valence electrons is not less than 4 using their enthalpy of atomisation. The glass transition temperature was found to increase with increase in Al content. The glass transition temperature is lower limit to crystallization temperature, and therefore increase in glass transition temperature and hence addition of Aluminium hints stability against spontaneous crystallization in modified phase change material.

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1. Introduction

A lot of attention has been devoted to characterization and improvement of the properties of chalcogenide glasses exhibiting the switching phenomenon. The glass transition temperature and the related nature of the chemical bond are important parameters for characterization of these glasses to explore their possible use as phase change memory material. This paper presents and discusses a model that can be used to estimate the glass transition temperatures of chalcogenide glasses in general and phase-change materials in particular. Since at normal heating rates amorphous materials generally crystallize just above the glass transition temperature, the glass transition temperature can be seen as a lower limit for the crystallization temperature. Crystallization below the glass transition temperature is extremely slow due to the high activation energy for atom movement. The glass transition temperature is therefore a good parameter for first-order estimation of the archival life stability of phase-change material. The model can be used to select and improve promising phase-change materials compositions with respect to their archival life stability.

2. Model for estimating glass transition temperature of amorphous materials

The Tg represents the temperature above which an amorphous matrix can attain various structural configurations and below which the matrix is frozen into a structure which cannot easily change to another structure. Therefore it is reasonable to assume that Tg must be related to the magnitude of the cohesive forces within the network since these forces must be overcome to allow for atom movement.

The most promising approach to predict glass transition temperatures, in which the chemical threshold is taken into account, seems to be to correlate Tg with the enthalpy of

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*Corresponding author: rthangaraj@rediffmail.com atomization[1]. By estimating the enthalpy of atomization of the glass from summing all individual bond enthalpies in the structure, one takes into account the fact that Tg increases both with increasing number of bonds and with increasing bond strength. Since hetero nuclear bonds have larger bond enthalpy than homo nuclear bonds, the enthalpy of atomization calculated in this way shows a maximum at the chemical threshold and therefore may be able to explain the features observed for Tg at the chemical threshold. Tichy and Ticha [2] showed by gathering experimental data for a large number of chalcogenide glasses that a linear relation between Tg and overall mean bond energy describes the data much better than in case when only the average coordination number is taken into consideration and no distinction is made between individual bond energies/enthalpies. In this paper the approach of Tichy and Ticha is used in order to be able to estimate the Tg of phase-change memory materials.

3. Calculating enthalpies of atomisation

The method used in this paper to calculate enthalpies of atomisation is based on the chemical bond approach of Bicerano and Ovshinsky [3]. This approach is applicable to glasses in which the bonding is predominantly covalent. Within the model, the following four assumptions are made.

(1) Each element in the covalent structure has a preferred coordination number ‘m’. For the elements from the VIB, VB and IVB groups of the periodical system the preferred coordination numbers are 2,3 and 4, respectively. These values satisfy the ‘8 - N’ rule, where N corresponds to the number of s,p-valence electrons. Applying the 8 - N rule to the elements from the groups IB– IIIB would result in coordination numbers larger than 4. This is not possible in a covalently bonded structure. To solve this problem, Liu and Taylor [4] proposed to assume that for the elements from group IB–IIIB formal charge transfer takes place from the chalcogen elements or, when not available, the group VB elements. This then leads to tetrahedral coordination for the group IB–IIIB elements and increased coordination for the group VIB or VB elements. The elements then satisfy the generalised ‘8 -< N>’ rule where <N> is the number of valence electrons formally assigned to the elements [4]. The average coordination number <m> can be calculated from the generalised 8 - <N> rule as follows:

$<m>= 8 - <n> = 8 - <N>$;

where <n> is the averaged number of valence electrons per atom in the glass composition. <n> equals the average number of formal valence electrons per atom <N> (i.e after charge transfer from chalcogen element to group IIIB element as proposed in previous paragraph) in the glass composition.

(2) Hetero nuclear bonds are preferred to homo nuclear bonds .

(3) Bonds are formed in the sequence of decreasing bond enthalpy (bond enthalpies are defined positive) until all available formal valences of the atoms are saturated and the total number of bonds divided by the number of atoms corresponds to <m>/2.

(4) Hetero nuclear bond enthalpies can be related to homo nuclear bond enthalpies using Pauling’s equation [5]:

$H_{AB}= (H_{AA} +H_{BB})/2 +96.14*(S_a-S_b)^2$

where H_{AA} and H_{BB} are the homonuclear bond enthalpies, H_{AB} is a heteronuclear bond enthalpy (in kJ/Mole) and S_a and S_b are the respective electronegativities of atoms A and B. Since Pauling did not provide the covalent bond enthalpies for bonds with the group IB–IIIB elements, values from literature are taken for calculation.

4. Relating enthalpies of atomisation to t_g-data

The overall empirical relation found between Tg (in Kelvin) and enthalpy of atomization Ha (kJ/Mole) is

$$T_g = 3.44H_a – 480 ;$$

The slope of 3.44 is in reasonable agreement with the value of 311 K/eV or 3.23 K/(kJ/g atom) found by Tichy and Ticha [2], who used a slightly different set of bond energies.

The model is capable of predicting trends in the glass transition temperature as a function of composition even for glasses containing metallic-like elements, as long as bonding is covalent.

COMPOSITIONS STUDIED

Al$_x$(GST)$_{1-x}$ X= 0.15, 0.20, 0.25, 0.30

C0 = Ge$_{0.22}$ Sb$_{0.22}$ Te$_{0.56}$
C1 = Al$_{0.15}$ (Ge$_{0.22}$ Sb$_{0.22}$ Te$_{0.56}$)$_{0.85}$ = Al$_{0.15}$ Ge$_{0.187}$ Sb$_{0.187}$ Te$_{0.476}$
= Al$_{0.15}$(IV) Ge$_{0.187}$ Sb$_{0.187}$ Te$_{0.15}$ (lll) Te$_{0.326}$ (ll)
C2 = Al$_{0.20}$ (Ge$_{0.22}$ Sb$_{0.22}$ Te$_{0.56}$)$_{0.80}$ = Al$_{0.20}$ Ge$_{0.176}$ Sb$_{0.176}$ Te$_{0.448}$
= Al$_{0.20}$ (lV) Ge$_{0.176}$ Sb$_{0.176}$ Te$_{0.20}$ (lll) Te$_{0.248}$ (ll)
C3 = Al$_{0.25}$ (Ge$_{0.22}$ Sb$_{0.22}$ Te$_{0.56}$)$_{0.75}$ = Al$_{0.25}$ Ge$_{0.165}$ Sb$_{0.165}$ Te$_{0.42}$
= Al$_{0.25}$ (lV) Ge$_{0.165}$ Sb$_{0.165}$ Te$_{0.25}$ (lll) Te$_{0.17}$ (ll)
C4 = Al$_{0.30}$ (Ge$_{0.22}$ Sb$_{0.22}$ Te$_{0.56}$)$_{0.70}$ = Al$_{0.30}$ Ge$_{0.154}$ Sb$_{0.154}$ Te$_{0.392}$
= Al$_{0.30}$ (lV) Ge$_{0.154}$ Sb$_{0.154}$ Te$_{0.30}$ (lll) Te$_{0.092}$ (ll)

Compositions	<N>	<m>	<m>/2
C0	5.34	2.66	1.33
C1	4.989	3.011	1.505
C2	4.872	3.128	1.564
C3	4.755	3.245	1.623
C4	4.638	3.362	1.681

Compositions	# Bonds	Fractional presence	Eab (KJ/Mole)	Energy in system(KJ/Mole)
C0	Te(ll)-Ge(lV) Te(ll)-Sb(lll) Sb(lll)-Sb(lll)	.88 .24 .21 Total=1.33	192.278 186.240 175	169.20 44.697 36.75 Total=250.647
C1	Te(ll)-Ge(lV) Ge(lV)-Te(lll) Te(lll)-Sb(lll) Sb(lll)-Al(lV) Al(lV)-Al(lV)	.652 .096 .354 .207 .196 Total=1.505	192.278 192.278 186.240 159.11 106	125.365 18.458 65.928 32.935 20.776 Total=263.462
C2	Te(ll)-Ge(lV) Te(lll)-Ge(lV) Te(lll)-Sb(lll) Al(lV)-Sb(lll) Al(lV)-Al(lV)	.496 .207 .393 .135 .3326 Total=1.564	192.278 192.278 186.24 159.11 106	95.369 39.801 73.192 21.479 35.2556 Total=265.096
C3	Te(ll)-Ge(lV) Ge(lV)-Te(lll) Te(lll)-Sb(lll) Sb(lll)-Al(lV) Al(lV)-Al(lV)	.34 .32 .432 .063 .468 Total=1.623	192.278 192.278 186.24 159.11 106	65.374 61.528 80.455 10.024 49.608 Total=266.989
C4	Te(ll)-Ge(lV) Ge(lV)-Te(lll) Te(lll)-Sb(lll) Te(lll)-Al(lV) Al(lV)-Al(lV)	.184 .432 .462 .006 .597 Total=1.681	192.278 192.278 186.24 174.58 106	35.379 83.064 86.0428 1.04748 63.283 Total=268.815

CALCULATION OF T$_G$

Composition	Energy of system in KJ/Mole	Calculated Tg as per Model (in K)
C0	250.647	382.225
C1	263.462	426.309
C2	265.096	431.930
C3	266.989	438.442
C4	268.815	444.723

Conclusion

A model is used for estimating glass transition temperatures of covalent amorphous materials which may include metallic-like elements from the groups IB–IIB. The model is based on the existence of a correlation between glass transition temperatures and enthalpies of atomisation. Enthalpies of atomisation are calculated by summing all individual bond enthalpies in the structure using a consistent basis set which is based on the enthalpies of atomisation of well-known compounds. The model can be applied to estimate the glass transition temperatures and related crystallization temperatures of promising phase-change compositions. It is found that the glass transition temperature increases by adding elements which increase atomic percentage of Aluminium in $Ge_2Sb_2Te_5$ due to increase in the average bond enthalpy.

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