Relation of coordination number to memory and threshold switching in chalcogenides

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Abstract. The paper reports a structural study of some memory and threshold chalcogenides in terms of coordination number C, defined by $C=8-N$, and is the average coordination number for covalently bonded materials. The average number of nearest neighbours surrounding a central atom, obtained for As–Ge–Te (memory) and Se–Ge–Te (threshold) systems have been used to estimate the cohesive energies, assuming simple additivity of bond energies. The bonding pattern so obtained, explains certain properties of these glasses.

1. Introduction

The recognition that chalcogenides were both understandable and potentially useful, stimulated an intense research effort. Insights have accumulated and continue to accumulate, as a result of interdisciplinary efforts involving theory and experimentation in diverse areas of physics, chemistry, electrical engineering and material science [1–5].

Considerations of the fundamental nature of chemical bonding in chalcogenide glasses, have been a very important part of this research effort [6–8]. A chemically ordered network model for the atomic arrangement in the glasses, wherein the maximum number of heteronuclear bonds are formed first and the remaining part of the valence requirement is met with by homonuclear bonding at random, was found to account satisfactorily, for the connectedness dependence of switching observed in As–Ge–Te and Se–Ge–Te chalcogenides. The amount of connectedness of an alloy determines whether it will have threshold or memory switching properties. It also explains the difference between them in terms of relative rigidities of atomic networks formed by different percentages of divalent, trivalent and tetravalent alloying elements. Weaker bonds and more flexible network containing an abundance of divalent atoms, provide lower energy barriers to reversible local order changes and structural phase transition, whereas more rigid threshold switches can undergo electronic transitions which are automatically reversed when applied voltage causing excitation is removed.

The approach through chemical bond studies suggested by Bicerano and Ovshinsky [9–10], has been used in present paper to study some chalcogenides. Results based on quantitative analysis suggest that coordination number is related to memory and threshold switching in chalcogenides.

2. Model

The chemical bond approach as suggested by Bicerano and Ovshinsky [9] is based on the following assumptions:

(i) There is normal structural bonding with preferred coordination number C for each element in an alloy. For example, $C(Ge)=4$; $C(As)=3$; and $C(Se)=C(Te)=2$. It is equivalent to neglecting dangling bonds, Van der Waals interactions and some other valence defects.

(ii) Atoms combine more favourably with atoms of different kind than with the same kind, which assumes maximum amount of chemical ordering possible. Here atoms with identical valencies are considered to be of same kind.

(iii) Bonds are formed in sequence of decreasing bond energy until all the available valencies are saturated provided $D(A-B) \gg D(A-C)$ (where D is bond energy), and on the other hand if $D(A-B)=D(A-C)$ the weighing factor $e^{D/kT}$ decides the ratio of bonds to be formed.

(iv) The bond energies $D(A-B)$ for heteronuclear bonds are calculated using the Paulings relation [11]

$$D(A-B)=[D(A-A).D(B-B)]^{1/2} + 30(x_A - x_B)^2 \qquad (1)$$

where $D(A-A)$ and $D(B-B)$ are the energies of homonuclear bonds [12] in kcal/mol and x_A and x_B are the electronegativities of atoms involved [13]. The values of x_A and $D(A-A)$ for alloys studied are listed in table 1.

The model as stated above clearly uses two sets of parameters, viz. coordination number C (a measure of connectedness) of the elements and the bond energy D between elements.

3. Results and discussion

The application of the method has been illustrated using threshold and memory materials $Se_{25}Ge_{20}Te_{75}$, $As_5Ge_{10}Te_{85}$ and $As_{15}Ge_{10}Te_{75}$ abbreviated as T, M1 and M2, respectively.

Table 1, enlists the types of bonds expected to occur in T, M1 and M2 together with their bond energies. The average number of neighbours for each type of central atom is listed in table 2. The cohesive energies (CE) calculated for these alloys and their constituent elements, assuming simple additivity of bond energies, are listed in table 3. The results are CE(T) = 2·10 eV/atom, CE(M1) = 1·65 eV/atom and CE(M2) = 1·72 eV/atom.

Table 1. Energies of bonds expected to occur in T, M1, M2 materials.

T		M1 and M2	
A–B	$D(A-B)$*	A–B	$D(A-B)$
Ge–Se	49·4	As–Ge	35·6
Ge–Te	35·5	Ge–Te	35·5
Te–Te	33·0	As–Te	32·7
		Te–Te	33·0

*kcal/mole.

Table 2. Average expected number of neighbours.

Central atoms	Its neighbours	Average number for material		
		T	M1	M2
As	Ge	—	3·0	1·51
	Te	—	—	1·49
Ge	Te	1·50	2·50	1·76
	As	—	1·50	2·24
	Se	2·50	—	—
Te	As	—	—	0·30
	Se	—	0·29	—
	Ge	0·45	1·71	0·23
	Te	1·45	—	1·47
Se	Ge	2·0	—	—
	Te	—	—	—

Table 3. Cohesive energies (CE) in eV/atom.

Material	C	CE_2^a	CE_1^b	Percentage
T	2·40	2·10	2·56	82·0
M1	2·25	1·65	2·43	67·9
M2	2·35	1·72	2·50	73·2
As	3·0	2·09	2·96	70·6
Ge	4·0	3·26	3·85	84·7
Te	2·0	1·43	2·23	64·2
Se	2·0	1·90	2·25	84·4

$^a CE_2$ = Cohesive energies of materials assuming additivity of bond energies.
$^b CE_1$ = Cohesive energies obtained by weighted averaging over the elements.
^{c} Percentage = $100 \times CE_2/CE_1$.

As observed from table 3 the magnitude of C and CE follow the same behaviour as would be expected from qualitative arguments concerning relative rigidities of the network containing different percentages of divalent, trivalent and tetravalent atoms i.e. the cohesive energy should increase/decrease with the increase/decrease in the coordination number.

The results of C and CE are also consistent with the general mechanism suggested for switching [8] which expects the threshold voltage for switching to decrease with increase in temperature and to increase with increase in coordination number.

On comparing calculated values of CE with those obtained by assuming that the actual CE values are weighted averages of CE values of elements listed in table 3, we find that the calculated values (2·10, 1·65 and 1·72 eV/atom) for T, M1 and M2 are 82%, 67·9% and 73·2% respectively.

Underestimation is expected from the fact that while assuming simple additivity of non-interacting bond pair in bond activity assumption, one neglects electron correla-
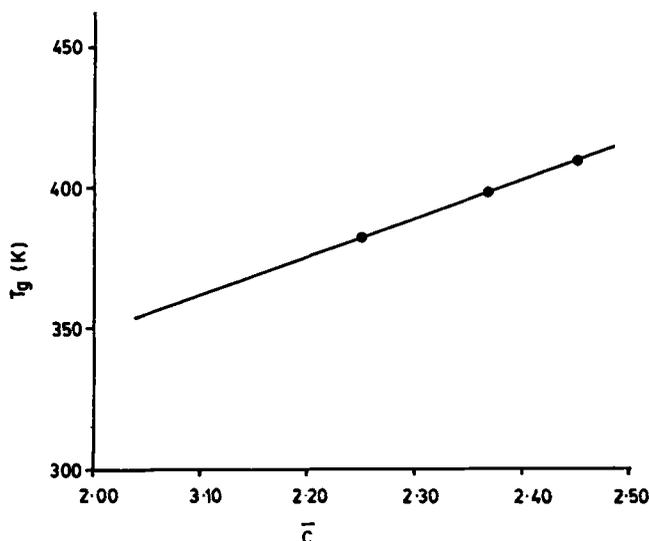
Figure 1. Demonstration of equation 2.

tion, self consistency and electron delocalization effects, which are the stabilizing effects. Further, the order of underestimation varies M1 > M2 > T. A similar trend of results was observed by Bicerano and Ovshinsky [9, 10] for materials $Se_{18}Ge_7$ $As_{35}Te_{40}$ (threshold), $Ge_{15}Te_{81}Sb_2S_2$ and $Ge_{24}Te_{72}Sb_2S_2$ (both memory type). The glass-transition temperature (T_g) was determined for the materials reported in this paper. The values are: $As_5Ge_{10}Te_{85}$ $(T_g = 383°C)$; $As_{15}Ge_{10}Te_{75}$ $(T_g = 398°C)$ and $Se_{25}Ge_{20}Te_{75}$ $(T_g = 413°C)$. Thus T_g increases in the same order as CE and C and the validity of the relation

$$T_g = T_g^0 + (C - 2)E_{04} \tag{2}$$

suggested by deNeufville and Rockstad [6] has been tested and demonstrated through figure 1.

Another observation about these glasses is that they all contain Te–Te bonds. An appreciable amount of Te–Te bonding is unavoidable for memory materials since Te atoms are present in large excess. Due to excess of Te content in the memory alloys the unswitched as well as the switched materials are dominated by Te-chains cross linked by tetravalent Ge atom which in turn are bridged by As atoms. However the length of exclusive Te chains in the unswitched material is likely to be smaller because its average coordination number has been found to be relatively large. A reduction in coordination number for switched materials coupled with an increase in Te contents, not only indicates the existence of relatively larger Te chains but also increases the possibility of formation of localized micro crystallites of Te.

Average coordination number (C) of a network may fundamentally be related to its vitrification properties. A bond percolation threshold C^P for average coordination number of the network is suggested. The materials above $C > C^P$ would be too rigid to set the memory transition. They would undergo threshold transition which does not require structural rearrangement.

The above study reveals that simple chemical bond considerations can be used to develop an understanding of structural properties of chalcogenide glasses.

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