

**COMMENTS ON SOME NUMERICAL PARAMETERS IN THE
ISOSTRUCTURAL
Sb₂S₃-As₂S₃-Sb₂Te₃ GLASSY SYSTEM**

K. N'DRI*, D. HOUPHOUËT-BOIGNY
Laboratoire de Chimie des Matériaux Inorganiques, UFR-SSMT, Université de Cocody,
22 B. P 582 Abidjan 22 (Côte d'Ivoire).

Binary Sb₂S₃-As₂S₃ and Sb₂Te₃-As₂S₃ glasses and a series of samples with the constant Sb₂Te₃ concentrations at 20 mol% and 40 mol% in the Sb₂S₃-As₂S₃-Sb₂Te₃ system have been synthesized. Their glass transition temperature (T_g) and optical gap (E_g) were also determined. The number of constraints per atom (N_{con}), the average coordination number (r), the number of lone-pair electrons (L), the average heat of atomization (H_s) and the overall mean bond energy (<E>) of each studied glass have been calculated. Correlations between the numerical parameter (H_s) and the experimental characteristics such as T_g and E_g have been discussed.

Received November 17, 2008; accepted November 20, 2008)

Keywords: Average mean coordination number, Number of lone-pair electrons,
Average heat of atomization, Overall mean bond energy.

1. Introduction

The properties of chalcogenide glasses in dependence on chemical composition are of interest, especially in considering the effects of average coordination number, number of covalent bonds per atom [1]. The structure of glasses is an important issue, knowledge of which is necessary for understanding the material's properties and also for the material engineering. Several structural models describing composition property relationship have been presented for some glasses. Most of these models are based on Phillips constraint theory [2,3] which predicts a transformation from underconstrained or floppy network to overconstrained or rigid network. Discontinuities in physical quantities like, for e.g., electrical switching field in Te-based chalcogenide glasses [4,5], Mössbauer site-intensity ratios [6], activation energies for viscosity and enthalpy relaxation near T_g [7], specific heat jumps at T_g [7] have been observed around r=2.4. Electrical switching studies on Al_{0.2}Ge_xTe_{0.8-x} revealed two thresholds, at r=2.50 and 2.65 [4,8]. Experiments on Al₂₀As_xTe_{80-x} glasses and As₄₀Te_{60-x}In_x showed only one threshold, occurring respectively at r=2.60 [9] and 2.70 [10, 11]. In Ge-As-Te system thresholds were identified at r=2.40 and 2.67 [4], based on electrical switching studies on Ge_{0.075}As_xTe_{0.925-x}. However there are systems which were exceptions to these conditions because it has been shown that most physical properties of As₄₀Se_xTe_(60-x)[7], As₄₀S_(60-x)Se_x and As₂₄S₇₆Se_y[12] glasses are not universal functions of the average coordination number, r. The present study has two objectives; the first is to determine the average coordination number (r) which is related to the number of lone-pair electrons (L) and the number of constraints (N_{con}), the average heat of atomization (H_s) and the overall mean bond energy (<E>) of a series of binary and ternary glasses of Sb₂S₃-As₂S₃-Sb₂Te₃

*Corresponding author: ezekmk@yahoo.fr

system; the second is to correlate Tg and Eg, interpreted [13], with the chemical composition using the average heat of atomization (Hs) based on chemical bonding aspect.

2. Experimental details

The composition of the studied glasses in $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ ternary system is formulated as followed: $\text{As}_{0.4x}\text{Sb}_{0.4(100-x)}\text{S}_{60}$ ($x=10, 40, 50, 75$ and 100) and $\text{As}_{0.4x}\text{Sb}_{0.4(100-x)}\text{S}_{0.6x}\text{Te}_{0.6(100-x)}$ ($x=50, 60, 80, 90$ and 100) respectively for $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$ and $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$ systems, $\text{As}_{0.4x}\text{Sb}_{0.4(100-x)}\text{S}_{48}\text{Te}_{12}$ ($x=10, 30, 45$ and 60) and $\text{As}_{0.4x}\text{Sb}_{0.4(100-x)}\text{S}_{36}\text{Te}_{24}$ ($x=10, 25$ and 40) respectively for sections with constant Sb_2Te_3 concentrations at 20 and 40mol% in the above ternary system. The samples were synthesized by melting the elemental components of high purity (99.999%) in evacuated silica tubes according to a technique reported previously [13]. Their thermal and optical properties of the quenched samples were determined and their glassy state was confirmed by X-ray diffraction at room temperature using the Cu-K α radiation [13].

3. Results and discussion

The parameters of binary glasses in $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$ and $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$ systems, as well as ternary glasses of 20 mol% and 40 mol% Sb_2Te_3 sections in $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ system such as average coordination number (r), number of constraints per atom (N_{con}), lone-pair electrons (L), parameter (R) determining the nature of chemical bonds in the glasses, average heat of atomization (H_s), overall mean bond energy ($\langle E \rangle$) have been calculated numerically. Values of the above parameters and those of thermal characteristic (T_g) of the studied glasses are listed in tables 1-4.

Table 1: Values of r , L , R , H_s , $\langle E \rangle$ and T_g for $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$ glassy system.

Composition	r	L	R	$H_s(\text{Kj/mol})$	$\langle E \rangle$ (eV)	T_g (K) [13]
$\text{As}_{04}\text{Sb}_{36}\text{S}_{60}$	2.4	3.2	1	272.351	2.464	493
$\text{As}_{10}\text{Sb}_{30}\text{S}_{60}$	2.4	3.2	1	274.714	2.446	491
$\text{As}_{20}\text{Sb}_{20}\text{S}_{60}$	2.4	3.2	1	278.652	2.414	487
$\text{As}_{30}\text{Sb}_{10}\text{S}_{60}$	2.4	3.2	1	282.590	2.382	485
$\text{As}_{40}\text{S}_{60}$	2.4	3.2	1	286.528	2.351	487

Table 2: Values of r , L , R , H_s , $\langle E \rangle$ and T_g for $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$ glassy system.

Composition	r	L	R	$H_s(\text{Kj/mol})$	$\langle E \rangle$ (eV)	T_g (K) [13]
$\text{As}_{20}\text{Sb}_{20}\text{S}_{30}\text{Te}_{30}$	2.4	3.2	1	254.772	2.452	440
$\text{As}_{24}\text{Sb}_{16}\text{S}_{36}\text{Te}_{24}$	2.4	3.2	1	261.133	2.446	443
$\text{As}_{32}\text{Sb}_8\text{S}_{48}\text{Te}_{12}$	2.4	3.2	1	273.826	2.434	458
$\text{As}_{36}\text{Sb}_4\text{S}_{54}\text{Te}_6$	2.4	3.2	1	280.177	2.427	462
$\text{As}_{40}\text{S}_{60}$	2.4	3.2	1	286.528	2.351	487

Table 3: Values of r , L , R , H_s , $\langle E \rangle$ and T_g for $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ glassy system (20 mol% Sb_2Te_3 section).

Composition	r	L	R	$H_s(\text{Kj/mol})$	$\langle E \rangle$ (eV)	T_g (K) [13]
$\text{As}_{04}\text{Sb}_{36}\text{S}_{48}\text{Te}_{12}$	2.4	3.2	1	262.800	2.477	471
$\text{As}_{12}\text{Sb}_{28}\text{S}_{48}\text{Te}_{12}$	2.4	3.2	1	265.950	2.465	470
$\text{As}_{18}\text{Sb}_{22}\text{S}_{48}\text{Te}_{12}$	2.4	3.2	1	268.312	2.455	466
$\text{As}_{24}\text{Sb}_{16}\text{S}_{48}\text{Te}_{12}$	2.4	3.2	1	270.676	2.446	461

Table 4: Values of r , L , R , H_s , $\langle E \rangle$ and T_g for Sb_2S_3 - As_2S_3 - Sb_2Te_3 glassy system (40 mol% Sb_2Te_3 section).

Composition	r	L	R	H_s (Kj/mol)	$\langle E \rangle$ (eV)	T_g (K) [13]
$As_{04}Sb_{36}S_{36}Te_{24}$	2.4	3.2	1	253.277	2.477	457
$As_{10}Sb_{30}S_{36}Te_{24}$	2.4	3.2	1	255.613	2.468	454
$As_{16}Sb_{24}S_{36}Te_{24}$	2.4	3.2	1	257.973	2.458	447
$As_{24}Sb_{16}S_{36}Te_{24}$	2.4	3.2	1	261.133	2.446	443

From the above tables, the contents of chalcogen atoms (S and Te) don't vary when the composition varies in binary system Sb_2S_3 - As_2S_3 and ternary system Sb_2S_3 - As_2S_3 - Sb_2Te_3 (containing constant Sb_2Te_3 concentrations at 20 and 40 mol%). This behaviour is not the same in Sb_2Te_3 - As_2S_3 system where variation of chalcogen content is observed. But in all studied glasses, the content of non-chalcogen atom As increases whereas that of Sb decreases (and vis-versa). The parameters, r , L and R aren't dependent on the compositions of the glasses because they have constant values. According to [14], $R=1$ is a point of the chemical threshold where usually maximal values of T_g are observed. In our case, this assertion is not verified because T_g does not vary with R in all studied cases as mentioned in tables 1-4. The other parameters such as H_s , $\langle E \rangle$ and T_g are influenced by glasses composition.

3.1 Bonding arrangement

It has been reported in previous work [15] that the structural network of Sb_2S_3 - As_2S_3 glasses mainly consists of the strongest Sb-S and As-S bonds, whereas that of Sb_2Te_3 - As_2S_3 glasses mainly consists of the strongest S-Te, Sb-S and As-S bonds. These glasses can be then regarded as stoichiometric compositions in which only the heteropolar bonds are present according to the Ordered Bond Network Model [15]. Applications of this model and the parameter R to the glasses of 20 mol% and 40 mol% Sb_2Te_3 sections in Sb_2S_3 - As_2S_3 - Sb_2Te_3 system lead us to suggest that these glasses are stoichiometric like those of the two binary systems because $R=1$. Their structure consists of S-Te, Sb-S and As-S bonds found in Sb_2Te_3 - As_2S_3 glasses.

3.2 Average coordination number and the number of constraints per atom

The concept of the average coordination number, r , is useful in describing the crosslinking in a covalently bonded solid. Phillips [2], Mott [16] and Flank et al. [17] have shown that the coordination number of covalently bonded atoms in glass is given by the 8-N rule where N is the number of the outer shell electrons. For a multicomponent chain forming chalcogenide glassy system, the average coordination number is defined simply as the atom averaged covalent coordination of the constituents [18]. The formula of the average coordination numbers of Sb_2S_3 - As_2S_3 and Sb_2Te_3 - As_2S_3 glasses have been previously reported [15]. That of Sb_2S_3 - As_2S_3 - Sb_2Te_3 ternary glasses (with constant Sb_2Te_3 concentrations at 20 and 40 mol %) formulated, is the same like the coordination number of Sb_2Te_3 - As_2S_3 glasses. The calculated value of the average coordination number of the latter glasses is equal to 2.4. These glasses have a two-dimensional character like those of Sb_2S_3 - As_2S_3 and Sb_2Te_3 - As_2S_3 systems. Their connectivity (or the dimensional network arrangement) is not changed in a continuous fashion by changing the non-chalcogen or the chalcogen (in the case of Sb_2Te_3 - As_2S_3 system) atoms content. In the other words, there is no transition structure in the glasses because no percolation occurs. On the basis of topological arguments counting constraints and the degrees of freedom, Phillips [2], Döhler et al [19] and Phillips and Thorpe [20] suggested that in covalent bonding of the studied glasses having $r=2.40$, the number of constraints equal to the number of degrees of freedom.

The invariability of the average coordination number can be explained, in each case of Sb_2S_3 - As_2S_3 - Sb_2Te_3 system, by the fact that As replaces Sb (both of them have the same coordination number equal to 3) and S (with a coordination number 2) replaces Te (which has the same coordination number). It is an isostructural substitution. The characteristics of the involved atoms are summarized in table 5 which indicates that, the non-chalcogen atoms (As and Sb) and the chalcogen atoms (S and Te) have the same valence electrons number equal to 5 and 6

respectively. They are isoelectronic elements. Invariability of r was observed in $As_{40}Se_xTe_{(60-x)}$ [7], $As_{40}S_{(60-x)}Se_x$ ($x=0, 15, 30, 45$ and 60) and $As_{24}S_{(76-y)}Se_y$ ($y=0, 19, 38, 57$ and 76) glasses [12].

Table 5. Atomic number, atomic configuration, valence electrons and coordination number of constituent elements of Sb_2S_3 - As_2S_3 - Sb_2Te_3 glasses.

Elements	As	Sb	S	Te
Atomic number	33	51	16	52
Atomic configuration	$[Ar]3d^{10}4s^24p^3$	$[Kr]4d^{10}5s^25p^3$	$[Ne]3s^23p^4$	$[Kr]4d^{10}5s^25p^4$
Valence electrons	5	5	6	6
Coordination number	3	3	2	2

Its values are 2.4 for $As_{40}Se_xTe_{(60-x)}$ and $As_{40}S_{(60-x)}Se_x$ glasses and 2.24 for those of $As_{24}S_{(76-y)}Se_y$ system when the selenium content increases. The scale classification of solids shown by figure 1 reproduced from S. A. Dembovskii [21], enables us to classify the two kind of above glasses between overconstrained amorphous ($3 \leq r \leq 4$) and underconstrained amorphous ($0 \leq r \leq 2$) because their coordination numbers are between 2 and 3. Because $r_{As}=r_{Sb}$ and $r_S=r_{Se}=r_{Te}$, $As_{40}Se_xTe_{(60-x)}$, $As_{40}S_{(60-x)}Se_x$, $As_{24}S_{(76-y)}Se_y$, Sb_2S_3 - As_2S_3 , Sb_2Te_3 - As_2S_3 , 20 mol% and 40 mol% Sb_2Te_3 sections of Sb_2S_3 - As_2S_3 - Sb_2Te_3 are isostructural systems according to A. K. Varshneya et al. [18]. The substitution occurs between two atoms having the same coordination number. Variations of the average coordination number have been observed and reported by several authors: $As_{40}Te_{60-x}In_x$ by B. H. Sharmila et al. [10] and J. T. Devaraju et al [11], $Ge_{20}Te_{80-x}Bi_x$ by Ambika and P. B. Barman [22], $Se_{0.75}Ge_{0.25-x}As_x$ by M. Fadel and S. S. Fouad [23], $Ge_{1-x}Sn_xSe_{2.5}$ by S. S. Fouad et al. [24], Sb_xSe_{1-x} by S. S. Fouad et al. [25] and $Ag_xTe_{50}As_{50-x}$ by S. M. El-Sayed et al. [26]. On the basis of [18] assertion, studied glasses by [10, 11, 22-26] are pure binary or ternary systems because the substitution is made between atoms which have different coordination numbers.

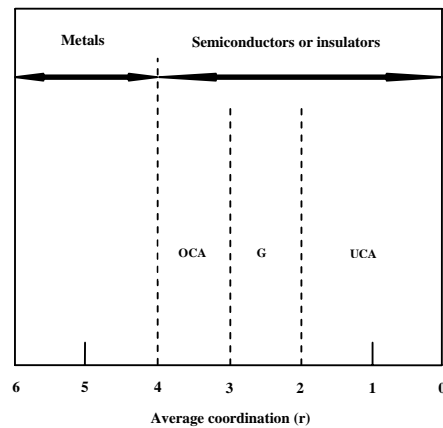


Fig. 1. r scale classification of solids [21] (OCA=Overconstrained amorphous, G=Glass and UCA=Underconstrained amorphous)

In a glassy system covalent networks can be mechanically constrained by interatomic valence forces such as bond stretching ($N_\alpha=r/2$) and bond bending ($N_\beta=2r-3$). Optimal glass formation is attained when the number of constraints N_{con} per atom is equal to the degrees of freedom (N_d) per atom i.e. for ideal glass $N_{con} = N_d$ [22]. The average number of constraints for compositions in our case is equal to 3 and its expression is:

$$N_{\text{con}} = N_{\alpha} + N_{\beta} \quad (1)$$

The glassy network is not influenced by mechanical constraints ($N_{\text{con}}=3$) because it does not vary in studied glasses of $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ system. In binary and ternary glasses of the above system, the substitution of Sb_2S_3 by As_2S_3 (or Sb by As) does not affect the number of constraints per atom. The strengths of the three bonds, predicted by the Ordered Bond Network Model [15], are nearly in the same order (189.02 KJ/mole for As-S, 199.11 KJ/mole for Sb-S and 200.26 KJ/mole for S-Te). The covalency of the network is not affected by the ionic interactions because of the existence of low electronegativity difference mainly between chalcogen and non-chalcogen atoms which can induce a neglected ionic character. This can't reduce the constraints and therefore, the condition $N_d=N_{\text{con}}=3$ can be met in these glasses. The mechanical stability is optimized and all glasses are the ideal.

3.3 Number of lone-pair electrons (L)

Chalcogenide glasses are often called lone pair semiconductors. L. Zhenhua [27] introduced a simple criterion for computing the ability of a chalcogenide system to retain its vitreous state; the criterion contains the number of lone-pair electrons which is necessary for obtaining the system in its vitreous state. The chemical bonds with lone-pair electrons are characterized by flexibility according Pauling [28]. The role of the lone-pair electrons consists of deforming the valence angles between the chemical bonds and smearing them out [29]. This flexibility relies on type, strength and concentration of the possibility existing chemical bonds in the glass. It is easier to deform a bond with lone-pair electrons than a bond with no unshared electrons. Structures with large number of lone-pair electrons are favour glass formation [22]. In order to calculate the number of lone-pair electrons in a chalcogenide glass system, the average coordination number proposed by Phillips [2] is introduced:

$$L=V-r \quad (2)$$

Where, L and V are the lone-pair electrons and valence electrons respectively. V for each glass is calculated by using the formula (3) for $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$ glasses and (4) for $\text{Sb}_2\text{Te}_3\text{-As}_2\text{S}_3$ glasses and $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ glasses containing 20 and 40 mol% of Sb_2Te_3 :

$$V_1=5X_{\text{As}}+5X_{\text{Sb}}+6X_{\text{S}} \quad (3)$$

$$V_2=5X_{\text{As}}+5X_{\text{Sb}}+6X_{\text{S}}+6X_{\text{Te}} \quad (4)$$

From the above expressions of valence electrons, X_{As} , X_{Sb} , X_{S} and X_{Te} are the atomic fractions of As, Sb, S and Te respectively. The calculated number of lone-pair electrons (L) of all glasses of $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ system by using equation (2) is constant and has a value equal to 3.2. It is clear that L does not vary with the increase in the content of any atom in the studied cases. By increasing the number of lone-pair electrons, the strain energy in a system decreases [30]. So, the strain energy in the case of binary and ternary studied glasses of $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ system, does not vary. L decreases continuously with the increase in the content of In, Bi and Sn respectively in $\text{As}_{40}\text{Te}_{60-x}\text{In}_x$ [10, 11], $\text{Ge}_{20}\text{Te}_{80-x}\text{Bi}_x$ [22] and $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_{2.5}$ [24] systems. The decrease in L, according to [24], is caused by the interactions between the Sn ion and the lone pair electrons of a bridging Se atom. The interaction decreases the role of lone-pair electrons in the glass formation when Sn content increases. In $\text{Se}_{0.75}\text{Ge}_{0.25-x}\text{As}_x$ and $\text{Ag}_x\text{Te}_{50}\text{As}_{50-x}$ systems studied respectively by [23] and [26], L increases with the increasing of As and Ag contents. This is caused by the interaction between Ag ion and lone-pair electrons of a Te atom [26]. The interaction increases the role of lone-pair electrons in the glass formation [27]. It was concluded from these results that some lone-pair electrons in the structure of a system are necessary condition for obtaining the system in vitreous state. In the cases of $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ glasses, the role of lone-pair electrons does not vary because L is invariable. This can be interpreted by the probably absence of interaction between lone-pair electrons of chalcogen atoms (S and Te) and non-

chalcogen (As and Sb) ions. According to Pauling's electronegativity scale, values for the atoms involved in our case are 2.18 for As, 2.05 for Sb, 2.58 for S and 2.10 for Te. The non-existent interaction between the non-chalcogen (Sb and As) ions and the lone-pair electrons of chalcogen atoms (S and Te) is due to the similar electronegativity of the constituent atoms of the glasses. Note that, the studied materials in $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ system are formed by only covalent bonds such as Sb-S, As-S and S-Te where the ionic character can be neglected. These bonds have lower ionicity. This explains why the lone-pair electron does not vary in each case of the $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ glasses. For a binary system the number of lone-pair electrons must be larger than 2.6 and for ternary system it must be larger than 1[27]. The obtained data of lone-pair electrons equal to 3.2 for studied glasses of $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ system agrees with the former suggestion given by [27]. Because for binary $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$ and $\text{As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ glasses and ternary $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ glasses (containing 20 and 40 mol% of Sb_2Te_3), lone-pair electrons is larger than 2.6 and 1 respectively. The lone-pair electron of $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_{2.5}$ system is between 1.801 and 2.853 [24]. This leads them to indicate that this system can form glass at the ordinary rate but SnSe can't form a glass at the ordinary rate because its lone-pair electrons is equal to 1.33. The lone-pair electrons ($L=3.2$) of our studied glasses being higher than that of S. S. Fouad et al. [24], can enable us to conclude that, the compositions of $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ system can form glass at ordinary rate.

3. 4 Average heat of atomization

The heat of atomization $H_s(\text{A-B})$ at standard temperature and pressure of a binary semiconductor formed from atom A and B is the sum of the heats of formation ΔH and the average of the heats of atomization H_s^A and H_s^B [31, 32]. $H_s(\text{A-B})$ corresponds to the average non-polar bond energy of the two atoms according L. Brewer [33] and can be expressed by:

$$H_s(\text{A-B}) = \Delta H + \frac{1}{2}(H_s^A + H_s^B) \quad (5)$$

In the above formula, ΔH is proportional to the square of the difference between the electronegativities χ_A and χ_B of the atoms A and B respectively:

$$\Delta H \propto (\chi_A - \chi_B)^2 \quad (6)$$

In the few materials for which it is known, the amount of heat of formation ΔH is about 10% of the heat of atomization and therefore neglected [34, 35]. Hence, $H_s(\text{A-B})$ is given quite well by:

$$H_s(\text{A-B}) = \frac{1}{2}(H_s^A + H_s^B) \quad (7)$$

The average heat of atomization of H_s is extended to ternary and higher-order semiconductor compounds and is defined as a direct measure of the cohesive energy and this of the average bond strength for $\text{A}_\alpha\text{B}_\beta\text{C}_\gamma$ compound as [24, 36]:

$$H_s = (\alpha H_s^A + \beta H_s^B + \gamma H_s^C) / (\alpha + \beta + \gamma) \quad (8)$$

This above formula has been applied to $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3$ glasses. $\text{As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ glasses and those of 20 mol% and 40 mol% Sb_2Te_3 sections in $\text{Sb}_2\text{S}_3\text{-As}_2\text{S}_3\text{-Sb}_2\text{Te}_3$ system are formed by four atoms: As, Sb, S and Te. Their compounds can be expressed as followed: $\text{A}_\alpha\text{B}_\beta\text{C}_\gamma\text{D}_\delta$ and the average heat of atomization is given by:

$$H_s = (\alpha H_s^A + \beta H_s^B + \gamma H_s^C + \delta H_s^D) / (\alpha + \beta + \gamma + \delta) \quad (9)$$

The results of the average heat of atomization of the above binary and ternary glasses, using the values of H_s for As, Sb, S and Te (301.42, 262.04, 276.6 and 197 KJ/mol respectively) are listed in tables 1-4. As shown in figure 2, the observed variation in average heat of atomization (H_s) can be considered as linear with substitution of Sb atoms for As atoms. The data obtained for H_s clearly

follow a partial atomic percentage as model. Thus the data for Hs and ψ_{As} (atomic percentage of As) of glasses can be related by the below expressions (10) for $Sb_2S_3-As_2S_3$, (11) for $Sb_2Te_3-As_2S_3$, (12) for 20 mol% of Sb_2Te_3 section and (13) for 40 mol% of Sb_2Te_3 section in $Sb_2S_3-As_2S_3-Sb_2Te_3$ system.

$$H_s = 0.3938 (\psi_{As} + 687.5952) \quad (10)$$

$$H_s = 1.5878 (\psi_{As} + 140.4560) \quad (11)$$

$$H_s = 0.3938 (\psi_{As} + 663.3438) \quad (12)$$

$$H_s = 0.3913 (\psi_{As} + 643.2706) \quad (13)$$

It should be noted that the Hs versus ψ_{As} is a system dependent straight line relationship. Hs decreases on the one hand from $Sb_2S_3-As_2S_3$ (0 mol% Sb_2Te_3) to $Sb_2Te_3-As_2S_3$ (0 mol% Sb_2S_3) and on the other hand, from $Sb_2S_3-As_2S_3$ to 20 mol% and 40 mol% Sb_2Te_3 sections in the ternary $Sb_2S_3-As_2S_3-Sb_2Te_3$ system. As the heat of atomization (Hs) can be correlated to the average bond strength, one can conclude that As_2S_3 increases the average bond strength of the studied glasses when its concentration increases in each binary system and in the two sections of ternary $Sb_2S_3-As_2S_3-Sb_2Te_3$ system. But Sb_2Te_3 decreases the average bond strength when its content increases from 0 mol% to 20 and 40 mol% sections as shown in figure 2.

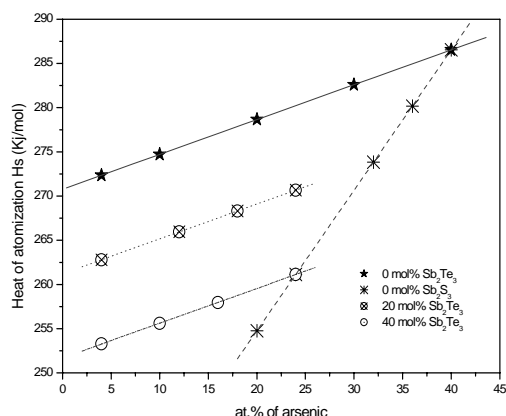


Fig. 2. Variation of Hs versus the atomic % of As in the $Sb_2S_3-As_2S_3$ (0 mol% Sb_2Te_3) and $Sb_2Te_3-As_2S_3$ (0 mol% Sb_2S_3) binary systems and in the $Sb_2S_3-As_2S_3-Sb_2Te_3$ ternary system at constant Sb_2Te_3 concentrations of 20 and 40 mol%.

The decreasing of Hs from $Sb_2S_3-As_2S_3$ (0 mol% Sb_2Te_3) system to $Sb_2Te_3-As_2S_3$ (0 mol% Sb_2S_3) system or from $Sb_2S_3-As_2S_3$ to 20 and 40 mol% of Sb_2Te_3 sections of $Sb_2S_3-As_2S_3-Sb_2Te_3$ system, is probably due to the presence of Te atoms which form an heteropolar (S-Te) bond with S atoms predicted by the Ordered Bond Model and the parameter (R) in these systems.

3. 5 Overall mean bond energy <E>

The properties of chalcogenide glasses are related to overall mean bond energy <E>, which is a function of the average coordination number r, the type of bonds and the bond energy. Using the correlation proposed by Tichý and Tichá [14], for chalcogenide rich system with correspondent composition $AxByCz$, the value of <E> can be given by the followed formula:

$$\langle E \rangle = E_{bi} + E_{abe} \quad (14)$$

E_{bi} being the mean bond energy of average cross linking per atom can be expressed by:

$$E_{bi} = P_r E_{ahbe} \quad (15)$$

The degree of cross linking (P_r) is formulated as:

$$P_r = (xZ_A + yZ_B)/(x+y+z) \quad (16)$$

E_{ahbe} is the average heteropolar bond energy and its expression is suggested to be:

$$E_{ahbe} = (xZ_A E_{A-C} + yZ_B E_{B-C})/(xZ_A + yZ_B) \quad (17)$$

Z_A and Z_B are the coordination number of A and B atoms. E_{A-C} and E_{B-C} are the heteropolar bond energy of A-C and B-C heteropolar bonds respectively and are calculated by applying Pauling's [37] relation. The average bond energy per atom of the remaining matrix, E_{abe} is defined by equation (18) where E_{C-C} is the homopolar bond energy between chalcogen-chalcogen atoms.

$$E_{abe} = (2(0.5r - P_r) E_{C-C})/r \quad (18)$$

The degree of cross linking (P_r), the average heteropolar bond energy (E_{ahbe}) and the average bond energy per atom of the remaining matrix (E_{abe}) have been extended to Sb_2Te_3 - As_2S_3 glasses and to those of 20 and 40 mol% Sb_2Te_3 sections in Sb_2S_3 - As_2S_3 - Sb_2Te_3 system. Their formula can be expressed as $AxByCzDt$ where A and B are non-chalcogen atoms, C and D are chalcogen atoms. Here A=As, B=Sb, C=S and D=Te. So P_r , E_{ahbe} and E_{abe} expressions for these glasses are respectively:

$$P_r = (xZ_A + yZ_B)/(x+y+z+t) \quad (19)$$

$$E_{ahbe} = (xZ_A E_{A-C} + yZ_B E_{B-C} + zZ_C E_{C-D} + tZ_D E_{D-C})/(xZ_A + yZ_B + zZ_C + tZ_D) \quad (20)$$

$$E_{abe} = [2(0.5r - P_r) / r] \times [E_{C-C} + E_{D-D}] \quad (21)$$

The expression of E_{ahbe} is written by taking into account the fact that these glasses are formed by heteropolar bonds Sb-S, As-S and S-Te only. The values of the overall mean bond energy $\langle E \rangle$ for the binary and ternary glasses of Sb_2S_3 - As_2S_3 - Sb_2Te_3 system are given in tables 1-4. Calculation of the overall mean bond energy $\langle E \rangle$ shows that, the average bond energy per atom of the remaining matrix E_{abe} is equal to zero because the term $2(0.5r - P_r)$ is equal to zero too for binary and ternary systems (where $r=2.4$ and $P_r=1.2$). In this case $\langle E \rangle = E_{bi}$ for all studied glasses. It means that the overall mean bond energy is equal to that of the heteropolar bonds previously predicted by the parameter R which determinates the nature of chemical bonds in these glasses. These results indicate an agreement with the Ordered Bond Network Model where the heteropolar bonds are favoured over the homopolar bonds [38]. Figure 3 indicates that the overall bond energies $\langle E \rangle$ of glasses of Sb_2Te_3 - As_2S_3 system (0 mol% Sb_2S_3) and 20 and 40 mol% Sb_2Te_3 sections are higher than that of Sb_2S_3 - As_2S_3 glasses (0 mol% Sb_2Te_3). The high values of $\langle E \rangle$ are probably due to the presence of S-Te bonds which are absent in Sb_2S_3 - As_2S_3 glasses. Note that, $\langle E \rangle$ decreases in each case when the atomic % of arsenic increases. The variation of $\langle E \rangle$ has values equal to 0.113 eV (0 mol% Sb_2Te_3), 0.103 eV (0 mol% Sb_2S_3), 0.031 eV (20 mol% Sb_2Te_3 section) and 0.019 eV (40 mol% Sb_2Te_3 section). In spite of the observed differences, it can be concluded that, the increasing (or decreasing) of atomic percentage of As (or Sb) doesn't modify highly the overall mean bond energy $\langle E \rangle$ values in Sb_2S_3 - As_2S_3 - Sb_2Te_3 glasses. The low variation

of $\langle E \rangle$ in glasses containing tellurium or not can be explained by the type of chemical bonds and their energy in the structure of glasses.

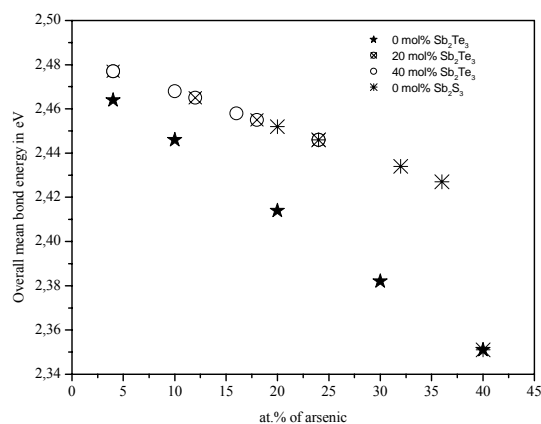


Fig. 3. Variation of $\langle E \rangle$ versus the atomic % of As in the $Sb_2S_3-As_2S_3$ (0 mol% Sb_2Te_3) and $Sb_2Te_3-As_2S_3$ (0 mol% Sb_2S_3) binary systems and in the $Sb_2S_3-As_2S_3-Sb_2Te_3$ ternary system at constant Sb_2Te_3 concentrations of 20 and 40 mol%

Because the heteropolar bonds (Sb-S, As-S and S-Te) forming the network of each glass have approximately the same energy according to the Ordered Bond Network Model [15].

3. 6 Relationship between Hs and glass transition temperature Tg

The heat of atomization Hs represents the average bond strength. Tg value of a glass represents the strength or the rigidity of the glass network. Greatest the Tg, greatest must be the rigidity of the medium [39, 40]. It is well established that Tg depends on the connectivity and consequently on the rigidity of the vitreous network. The factors that affect this rigidity are, for example, the type of the structural units that form the network according to A. K. Varshneya et al [18]. Interesting relationships in chalcogenide glasses such as those between the glass transition temperature and the electrical band gap [41], the glass transition and atomization energy [42] and the glass transition temperature and the optical gap [43] have already been demonstrated using the point of view of chemical bonding. Linke [44] assumed that the mean atomization enthalpy, $\langle Ha \rangle$, reflects the cohesive forces which be overcome to reach Tg and consequently Tg should be related to $\langle Ha \rangle$. For certain classes of glasses, Linke found $Tg \propto \langle Ha \rangle$. Figure 4 shows the variation of the heat of atomization (Hs) versus the glass transition temperature (Tg). For $Sb_2S_3-As_2S_3$ glasses and those of 20 and 40 mol% Sb_2Te_3 sections of $Sb_2S_3-As_2S_3-Sb_2Te_3$ system, Hs decreases when Tg increases. It means that the heat of atomization or the average bond strength decreases when the rigidity of the glass network increases. So at the higher value of Hs corresponds to the lower value of Tg and vis-versa in each case. Note that, Hs and Tg decreases from 0 mol% Sb_2Te_3 to 20 and 40 mol% Sb_2Te_3 sections. The increasing of Sb_2Te_3 concentration decreases Hs and the rigidity of glass network. The same behaviour is observed in the $(As_{30}Sb_{15}Se_{55})_{10-x}Te_x$ thin films when the content of Te increases [45].

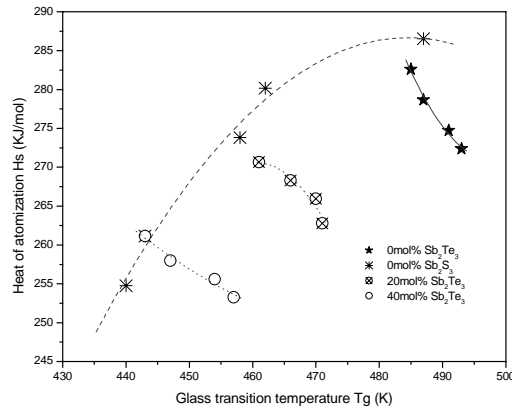


Figure 4: Variation of heat of atomisation H_s with the glass transition temperature T_g in the $Sb_2S_3-As_2S_3$ (0 mol% Sb_2Te_3) and $Sb_2Te_3-As_2S_3$ (0 mol% Sb_2S_3) binary systems and in the $Sb_2S_3-As_2S_3-Sb_2Te_3$ ternary system at constant Sb_2Te_3 concentrations of 20 and 40 mol%.

In the case of $Sb_2Te_3-As_2S_3$ glasses both H_s and T_g increase indicating that the average bond strength (H_s) increases when the rigidity of glass network increases. P. Sharma et al. [46] observed this behaviour in $Ge_{20}Se_{80-x}Bi_x$ system. On the basis of D. Linke assertion, $T_g \propto \langle Ha \rangle$, we can conclude that T_g can't be used to represent H_s and vis-versa in $Sb_2S_3-As_2S_3$ system and at constant Sb_2Te_3 concentrations of 20 mol% and 40 mol% in the $Sb_2S_3-As_2S_3-Sb_2Te_3$ system. In $Sb_2Te_3-As_2S_3$ system, T_g can be used to represent H_s and vis-versa because the two parameters show the same trend.

3.7 Relationship between the optical gap E_g and H_s

In chalcogenide glasses containing a high concentration of a group VI (Te or S) element the lone-pair electrons form the top of the valence band and the antibonding band forms the conduction band [47, 48]. It is therefore interesting to relate the optical gap with the chemical bond energy, and the parameter we use to specify the bonding is H_s . The relation between the energy gap and the average heat of atomization was discussed by Aigrain et al [49]. According their study a linear correlation exists and can be expressed for the semiconductors of diamond and zinc-blende structure by:

$$\Delta E = a (H_s - b) \quad (22)$$

Where a and b are characteristics constants. It is suggested from the above equation that the average heat of atomization is a measure of the cohesive energy and represents the relative bond strengths, which in turn is correlated with the energy gap of isostructural semiconductors. In $Sb_2S_3-As_2S_3$ and $Sb_2Te_3-As_2S_3$ systems, an increase in E_g with H_s is observed. But E_g is nearly constant while H_s increases in 20 mol% Sb_2Te_3 section of concerning $Sb_2S_3-As_2S_3-Sb_2Te_3$ system (figure 5). Note that, variation of optical gap (E_g) of the above binary systems has been previously reported [13].

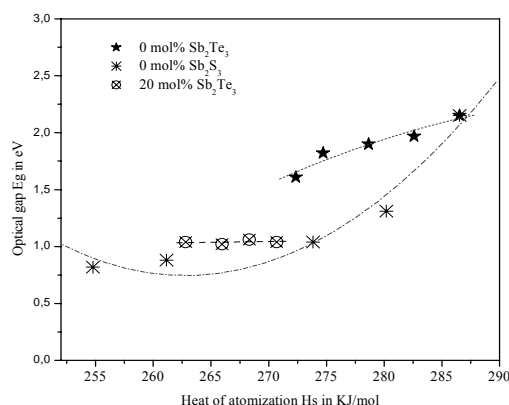


Fig. 5. Variation of optical gap E_g versus heat of atomisation H_s in the Sb_2S_3 - As_2S_3 (0 mol% Sb_2Te_3) and Sb_2Te_3 - As_2S_3 (0 mol% Sb_2S_3) binary systems and in the Sb_2S_3 - As_2S_3 - Sb_2Te_3 ternary system at constant Sb_2Te_3 concentration of 20 mol%

The latter observations in figure 5 enable us to suggest that, H_s can be used to represent E_g and vis-versa in binary systems mentioned above because these parameters (E_g and H_s) show a similar trend. It's not the case of 20 mol% Sb_2Te_3 section of Sb_2S_3 - As_2S_3 - Sb_2Te_3 system. The H_s effect on E_g is shown in figure 5. According to [47, 48], E_g for overconstrained materials with higher connectivity, $4 \geq r \geq 3$, depends more strongly on H_s than for glasses with lower connectivity, $3 \geq r \geq 2$. Even if all studied glasses have low connectivity ($r=2.4$), one can suggest that H_s has a high effect on E_g in Sb_2S_3 - As_2S_3 and Sb_2Te_3 - As_2S_3 systems. It is possible to conclude that the main factor determining E_g of these glasses can be the average heat of atomization (H_s) which represents the average bond strength. It is not the case of 20 mol% Sb_2Te_3 section of Sb_2S_3 - As_2S_3 - Sb_2Te_3 system where H_s has no effect on E_g because the latter parameter is invariable when H_s increases.

4. Conclusions

In this paper, we have shown that the average coordination number (r), the number of constraint per atom (N_{con}) and the number of lone-pair electrons (L) are invariable when Sb atoms are substituted by As atoms. The same behaviour is not observed in the case of the average heat of atomization (H_s) which increases as a function of the atomic percentage of As in the binary systems (Sb_2S_3 - As_2S_3 and Sb_2Te_3 - As_2S_3) and in the ternary Sb_2S_3 - As_2S_3 - Sb_2Te_3 (at 20 mol% and 40 mol% Sb_2Te_3 sections). Correlations between on the one hand T_g and H_s , on the other hand between E_g and H_s have shown good relationships because H_s can be used to represent T_g and vis-versa for Sb_2Te_3 - As_2S_3 glasses. H_s can also be used to represent E_g and vice-versa for binary systems (Sb_2S_3 - As_2S_3 and Sb_2Te_3 - As_2S_3). In the case of 20 mol% Sb_2Te_3 section of Sb_2S_3 - As_2S_3 - Sb_2Te_3 system, H_s can't be used to represent T_g (or E_g) because the parameters haven't the same trend.

References

- [1] E. Skordeva, D. Arsova, J. Non-Cryst. Solids, **192-193**, 665 (1995).
- [2] J. C. Phillips, J. Non-Cryst. Solids **34**, 153(1979)-181.
- [3] J. C. Phillips, J. Non-Cryst. Solids **43**, 37(1981).
- [4] R. Aravinda Narayanan, S. Asokan, A. Kumar, Phys. Rev. **B 54**, 4413(1996).
- [5] R. Aravinda Narayanan, S. Asokan, A. Kumar, Phys. Rev. **B 63**, 092203(2001).
- [6] W. Bresser, P. Boolchand, P. Suranyi, Phys. Rev. Lett. **56**, 2493(1986).
- [7] M. Tatsumisago, B. L. Halfpap, J. L. Green, S. M. Lindsay, C. A. Angell, Phys. Rev. Lett. **64**, 1549(1990).
- [8] R. Aravinda Narayanan, A. Kumar, Phys. Rev. **B 60**, 18599(1999).
- [9] S. Murugavel, S. Asokan, J. Mater. Res. **13**, 2992(1998).
- [10] B. H. Sharmila, J. T. Devaraju, S. Asokan, J. Non-Cryst. Solids **303**, 372(2002).
- [11] J. T. Devarju, B. H. Sharmila, S. Asokan, K. V. Acharya, Appl. Phys. **A 75**, 515(2002).
- [12] C. Lopez, K. A. Richardson, S. Seal, A. Shulte, C. Rivero, A. Villeneuve, A. Saliminia, J. Laniel et al., J. Amer. Ceram. Soc. **85**, 1372(2002).
- [13] N. Kouamé, J. Sei, D. Houphouët-Boigny, G. Kra, J.-C. Jumas, J. Olivier-Fourcade, C. R. Chimie **10**, 498(2007)-501.
- [14] L. Tichý, H. Tichá, J. Non-Cryst. Solids **189**, 144(1995).
- [15] K. N'Dri, J. Sei, D. Houphouët-Boigny, J. C. Jumas, Chalc. Lett. **4(9)**, 104(2007).
- [16] N. F. Mott, Philos. Mag. **19**, 835(1969)-852.
- [17] A. M. Flank, D. Bazin, H. Dexpert, P. Lagarde, C. Mervo & J. Y. Barraud, J. Non-Cryst. Solids **91**, 306(1987)-314.
- [18] A. K. Varshneya, A. N. Sreeram, D. R. Swiler, Physics and Chemistry of Glasses **34(5)**, 180(1993).
- [19] G. H. Döhler, R. Dandoloff & H. Biltz, J. Non-Cryst. Solids **42**, 87(1980)-96
- [20] J. C. Phillips & M. F. Thorpe, Solid State Commun. **53(8)**, 699(1985)-702.
- [21] S. A. Dembovskii, Izv. Akad. Nauk SSSR Neorg. Mater. **14**, 803(1978).
- [22] Ambika and P. B. Barman, Journal Ovonic Research **3(1)**, 21(2007).
- [23] M. Fadel and S. S. Fouad, Journal of Materials Science **36**, 3667(2001)-3673.
- [24] S. S. Fouad, S. A. Fayek and M. H. Ali, Vaccum **49(1)**, 29(1998).
- [25] S. S. Fouad, A. H. Ammar and M. Abo-Gbazala, Vaccum **48(2)**, 183(1997).
- [26] S. M. El-Sayed, H. M. Saad, G. A. Amin, F. M. Hafez, M. Abd-El-Rahman, Journal of Physics and Chemistry of Solids **68**, 1041(2007).
- [27] L. Zhenhua, J. of Non-Cryst. Solids **127**, 298(1991).
- [28] L. Pauling, The Nature of the Chemical Bond, 3rd Edition, cornell University Press, Ithaca, NY, p. 188, (1960).
- [29] R. Aravinda Narayanan, J. Non-Cryst. Solids **318**, 219(2003).
- [30] Achamma George, D. Sushamma, P. Predeep, Chalc. Lett. **3(4)**, 33(2006).
- [31] L. Pauling, J. Phys. Chem. **58**, 662 (1945).
- [32] L. Pauling, The Nature of the Chemical Bond, 3rd Edition, cornell University Press, Ithaca, NY, p. 180, (1960).
- [33] L. Brewer, Electronic Structure and Alloy Chemistry of the Transition Elements, ed. P. A. Beck. Interscience, New York, p. 222, (1963).
- [34] S. S. Fouad, Vaccum **52**, 506(1999)-507.
- [35] S. S. Fouad, A. H. Ammar, M. Abo-Ghazala, Physica **B 229**, 249(1997).
- [36] V. Sadagopan, H. C. Gotos, Solid State Electron **8**, 529 (1965).
- [37] L. Pauling, The Nature of the chemical bonds, Cornell University Press, 3rd ed., pp. 85, 92, (1960).
- [38] S. Mahadevan, A. Giridhar, A. K. Singh, J. Non-Cryst. Solids **103**, 179(1988).
- [39] E. A. Dimarzio, J. H. Gibbs, J. Polym. Sci. **60**, 121 (1959).
- [40] J. H. Gibbs, E. A. Dimarzio, J. Chem. Phys. **28**, 373 (1958).
- [41] M. Nunoshita and H. Arai, Solid State Commun. **11**, 213(1972).
- [42] A. Feltz, H. J. Buttner and W. Maul, J. Non-Cryst. Solids **8-10**, 64(1972).

- [43] J. P. Deneufville, H. K. Rockstad, *Amorphous and Liquid Semiconductors*, eds J. Stuke and W. Brening-Taylor and Francis Ltd, London, p. 419, (1974).
- [44] D. Linke, *Proc. 11th Int. Conf. on Glass*, Vol. 1, ed. J. Götz, Prague, p. 149, (1977).
- [45] A. A. Othman, K. A. Aly, A. M. Abousehly, *Thin Solids Films* **515**, 3507(2007)-3512.
- [46] P. Sharma, M. Vashistha, I. P. Jain, *Chalc. Let.* **2**(1), 115(2005)-121.
- [47] M. Kastner, *Phys. Rev. Lett.* **28**, 355(1972).
- [48] M. Kastner, *Phys. Rev.* **B 7**, 5237(1973).
- [49] C. Benoit, P. Aigrain, M. Balkanski, *Selected Constants Relative to Semiconductors*, Pergamon Press, New York, 1960.