CORRELATION OF THE GLASS TRANSITION TEMPERATURE AND AVERAGE ENERGETIC CONNECTIVITY IN NETWORK CHALCOGENIDE GLASSES

Mykhaylo Shpotyuk[1], Oleh Shpotyuk[2-4]

[1] Lviv Polytechnic National University, Lviv, Ukraine
[2] Vlokh Institute of Physical Optics, Lviv, Ukraine
[3] R&D Enterprise "Electron-Carat", Lviv, Ukraine
[4] Jan Długosz University in Częstochowa, Czestochowa, Poland
mykhailo.v.shpotiuk@lpnu.ua, shpotyukmy@yahoo.com
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Abstract: A correlation ratio between a glass transition temperature T_g and average bond energy E (obtained for chalcogenide glasses in L. Tichý & H. Tichá [J. Non-Cryst. Solids, 189, 1995]) was critically analyzed in this paper. As a result, this ratio was shown to have been obtained using incorrect calculations of the average bond energy E through inappropriate application of different averaging procedures for different terms of this parameter and, therefore, it cannot be used in practice. A mathematical algorithm for calculating the average energy bonding was adjusted by the atom-averaging procedure for the both energy of the "network part of a matrix" E_c (energy of heteropolar bonds) and energy of a "residual matrix" E_{rm} (energy of homopolar bonds), as well as considering the impossibility of forming covalent chemical bonds between cations of different type. It was stated that the linear ratio between the glass transition temperature T_g and energy bonding E can be obtained by the ratio $T_g \cong 326 \cdot (E - 0.94)$ and this claim was proved for 145 typical representatives of the covalent-bonded network chalcogenide glasses (Ge-As-S/Se-type systems).

Key words: chalcogenide glass, glass transition temperature, average bond energy, covalent network.

1. Introduction

A glass transition temperature T_g is one of the most important characteristics of chalcogenide glasses (ChG) [1, 2], that is, vitrified materials produced by the fast melt quenching [3–5]. Because of the wide usage of these disordered solids, determation and correct understanding of the composition changes and their correlation with other properties of covalent materials [4–6], for example, average coordination value Z, the energy of the covalent bond of glass network etc is extremely important.

The glass transition temperature T_g is the evidence of the beginning of the process of reorientation of some soft formations of a glass network when their viscosity begins to excess a critical value of 10^{13} P [7]. In general, changes in T_g are determined by the superposition of stronger covalent bonds, forming such structures, with weaker secondary bonds (intermolecular or the Van der Waals bonds), determining their mobility in the region of transition "glass – supercooled liquid". This concept allows predicting composition changes in T_g depending on average bond energy calculated per one atom of a structural unit. In [7], the equation was obtained for describing the interconnection between T_g and the mean coordination number Z (in the range $1 \le Z \le 2.7$) in the ChG:

$$\ln(T_g) = 1.6 \cdot Z + 2.3 . \qquad (1)$$

However, the obtained dependence cannot be proved experimentally for many "classical" ChG systems (e.g., As-S [4], As-Se [4, 8–11], Ge-S [4, 12], Ge-Se [4, 8, 13]) in which a decrease in T_g is observed with an increase in Z after stoichiometry.

In [14], with the use of the approach of covalent bonds developed initially in [6], a simple equation for describing the correlation between the glass transition temperature T_g[K] and an average bond energy or, in other words, energy bonding E[eV] (averaging data for 186 ChG representatives possessing covalent bonding) was obtained:

$$T_g \cong 311 \cdot (E - 0.9). \qquad (2)$$

Within this approach [14], E is calculated as a sum of average energy of a "network part of a matrix" E_c (heteropolar bonds) and average bond energy of a "residual matrix" E_{rm} (energy of homopolar bonds).

In spite of the wide usage of this equation for different ChG systems (e.g., [15–20]), the correctness of the proposed calculation method was not proved, let alone checking its general concepts. The algorithm of calculating E given in [14] is usually simply copied without doubting its correctness.

In this work the authors wish to analyse and, if necessary, adjust the approach to the calculation of the average bond energy E for ChG proposed in [14] and, on its basis, correctly parametrize the equation describing the correlation between the glass transition temperature T_g and average bond energy E.

2. Technique for calculating average bond energy E

For ChG systems whose structure can be described by so called "chain crossing model" [21] or model of chemically-ordered covalent network (COCN) [22], numerical calculation of E can be carried out on the basis of simple statistical taking into account the frequency of occurring different chemical bonds in the structure, as it was shown in [10]. For example, average energy E for As_xSe_{1-x} ChG can be estimated by the analysis of close environment of Se and As atoms for chosen composition with the use of energy of chemical bonds obtained by Pauling (E_{Se-Se}=184 kJ/mol, E_{As-Se}=174 kJ/mol, E_{As-As}=134 kJ/mol) [23]. No doubt, the values of energy E obtained by this approach should match those calculated according to [14], but it was not observed in practice.

In general, real values of average bond energy (following the example of ChG of A_xC_{1-x} binary system, where A is a cation and C is a chalcogen) averageing by one atom of the formula glass unit, can be obtained on the basis of known distribution of covalent chemical bonds within a COCN model:

$$E = Z/2 \cdot (n_{A-A} \cdot E_{A-A} + n_{A-C} \cdot E_{A-C} + \\ + n_{C-C} \cdot E_{C-C}) \quad , \quad (3)$$

where n_{A-Ch}, n_{A-A} i n_{C-C} are parts of hetero-(A-C) and homeopolar (A-A i C-C) bonds, respectively ($n_{A-C} + n_{A-A} + n_{C-C} = 1$).

In more general case, for compositionally norma-lized ChG of ternary system $A_xB_yC_z$ ($x+y+z$=1), containing one type of chalcogen C (with the coordination r_C=2) and two types of different cations A and B (with coordinations r_A and r_B, respectively), an average coordination number Z equals

$$Z = (xr_A + yr_B + zr_C)/(x + y + z) = \\ = xr_A + yr_B + (1 - x - y)r_C \quad . \quad (4)$$

In this case, the average number of covalent bonds per one atom equals $Z/2$, since each bond "belongs" to both atoms forming it.

As it was shown above, the approach described in [14] assumes that E is calculated as a sum of average bond energy of a "network part of the matrix" E_c and average bond energy of a "residual matrix" E_{rm}:

$$E = E_c + E_{rm} . \quad (5)$$

These energy summands can be calculated by the appropriate formulae according to the stoichiometry ratio, introduced in [14]:

$$R = \frac{zr_C}{xr_A + yr_B} = \frac{2(1 - x - y)}{xr_A + yr_B} . \quad (6)$$

R=1 corresponds to stoichiometric ChG, formed exclusively including the most energetically advanta-geous heteropolar bonds; when R>1, it is a case of undercoordinated (chalcogen enriched) ChG; if R<1, the case of over coordinated (chalcogen depleted) ChG is observed, in which homeopolar cation – cation bonds dominate.

The energy of the "network part of the matrix" E_c can be considered to be a contribution of the heteropolar bonds:

$$E_c = P_r \cdot E_{hb} \text{ for } R\text{>}1, \quad (7)$$

$$E_c = P_p \cdot E_{hb} \text{ for } R\text{<}1, \quad (8)$$

where E_{hb} is an average energy of the heteropolar bonds (bonds A-C and B-C with respective energies E_{A-C} and E_{B-C}) belonging to one atom

$$E_{hb} = \frac{xr_A E_{A-C} + yr_B E_{B-C}}{xr_A + yr_B} , \quad (9)$$

and P_r i P_p are degrees of cross-linking:

$$P_r = \frac{xr_A + yr_B}{x + y + z} = xr_A + yr_B , \quad (10)$$

$$P_p = \frac{zr_C}{x + y + z} = 2(1 - x - y), \quad (11)$$

By analogy, the average energy of the bonds of the "residual matrix" E_{rm} in [14] was determined as a contribution of the homeopolar covalent bonds (inclu-ding bonds of "chalcogen-chalcogen" C-C and "cation-cation" A-A and B-B kind with corresponding energies E_{C-C}, E_{A-A} and E_{B-B})

$$E_{rm} = 2\left(\frac{Z}{2} + P_r\right)E_{C-C}\bigg/Z \text{ for } R\text{>}1, \quad (12)$$

$$E_{rm} = 2\left(\frac{Z}{2} + P_p\right)E_{<\,>}\bigg/Z \text{ for } R\text{<}1, \quad (13)$$

where the arithmetic average of all potentially possible cation bonds was used as the energy of cation bonds $E_{<>}$

$$E_{<\,>} = \frac{E_{A-A} + E_{B-B} + E_{A-B}}{3} . \quad (14)$$

This approach is evidently incorrect due to two causes. First, if the chalcogen in ChG is depleted, the chemical bonds between the cations of one kind mostly

occur, that is, direct covalent chemical bonds between cations of different kind in ChG are not practically realized [4]. Moreover, the average energy of the bonds of "cation-cation" kind will considerably depend on the ratio between the content of the cations of different kind in the ChG matrix. For example, in the cases, when the network contains equal amount of arsenic As and germanium Ge, and when the number of one of the cation kind is scanty comparing with other, the average energy of the bonds of the "cation-cation" kind will be also different. Due to this, for eliminating drawbacks mentioned above, we propose considering the possibility of forming only the bonds A-A and B-B, and, for calculating the energy of cation bonds $E_{<>}$, using the following formula instead of equation (14):

$$E_{<\ >} = \frac{x r_A E_{A-A} + y r_B E_{B-B}}{x r_A + y r_B}. \qquad (15)$$

Second, for the correct numerical evaluation, according to equation (5), the average bonding E should contain two summands, which are averaged in the same way. In equations (7) and (8), the calculation of the average energy of the "network part of the matrix" E_c is carried out according to the total number of the atoms of the network. At the same time, the calculation of the average of the "residual matrix" E_{rm} in equations (12) and (13) is carried out according to the total number of the chemical bonds in the network.

Since the chemical composition of the ChG in the most cases is normalized by 1 ($x+y+z=1$), and the value of Z always exceeds 2 (except the ChG, formed only from the chalcogen atoms, for which $Z=2.0$), the average energy E calculated according to algorithm introduced in [14] will be systematically understated, which will cause obtaining overstated values of T_g as a result of using equation (2).

For example, for binary ChG, the correct final values for the average energy bonding E, calculated in this way, can be obtained only for the stoichiometric composition (where, in the frame of COCN, there is no homeopolar bonds at all) and glass, where the general number of bonds per atom (i.e., $Z/2$) approximates to the overal number of atoms which is possible only for glass made exclusively from chalcogen atoms. At the same time, the most essential mistakes while calculating E, are expected for the ChG with the maximally depleted chalcogen. It means that the error will increase with the deviation from the stoichiometry to the region of cation-enriched compositions.

Under such conditions, we propose using the following equations for calculating E_{rm} instead equations (12) and (13):

$$E_{rm} = \left(\frac{Z}{2} + P_r\right) E_{C-C} \quad \text{for } R>1, \qquad (16)$$

$$E_{rm} = \left(\frac{Z}{2} + P_p\right) E_{<\ >} \quad \text{for } R<1. \qquad (17)$$

It can be easily shown that the meanings of the average bond energy obtained by such an algorithm will coinside with those obtained experimentally. For example, in the case of $As_x Se_{1-x}$ ChG system, the calculated values of E fully coinside with those determined on the basis of statistic taking into account different possible structural units in [10].

3. Peculiarities of analytical description of correlation of glass transition temperature T_g and average energetic bonding E in mesh ChG

For checking the proposed approach, well-known literature data concerning the values of glass transition temperature T_g for 145 different chemical compositions of binary and ternary ChG systems of Ge-As-S/Se type (in particular, As-S (9 compositions) [4], As-Se (24 compositions) [4, 8–11], Ge-S (19 compositions) [4, 12], Ge-Se (26 compositions) [4,8,13], Ge-As-S (19 compositions) [24], $Ge_x As_y Se_{1-x-y}$ (18 compositions) [25], $Ge_x As_x Se_{1-2x}$ (30 compositions) [26]) were used.

The authors have limited sulfide and selenitic ChGs containing atoms of Ge and As as cations to those whose structure corresponds to the COCN model (without taking into account ChGs whose structure is determined by the "valence shell model" [27] or ChG on the basis of phosphorus P with double covalet bonds [4]). As a rough approximation, we assumed that the glass transition temperature T_g is a linear function of the average bonding energy according to a correlation:

$$T_g = a \cdot (E - b), \qquad (18)$$

where a[K/eB] and b[eB] are some coefficients.

Composition dependencies of the glass transition temperature T_g on the change of average bond energy E for ChG systems described above in the frame of the COCN model are shown in Figure 1. Points of different form and colour correspond to experimental data for the ChG of different systems matching with energies E calculated according to the algorithm introduced in Section 2.

For calculations the following values of energies of covalent bonds are used: E_{Se-Se}=184 kJ/mol, E_{S-S}=213 kJ/mol, E_{As-Se}=174 kJ/mol, E_{As-S}=189 kJ/mol, E_{Ge-Se}=207 kJ/mol, E_{Ge-S}=224 kJ/mol, E_{As-As}=134 kJ/mol, E_{Ge-Ge}=157 kJ/mol. Dotted lines in Fig.1 are used for visual demonstration of linear dependencies obtained by the method of mathe-matical adjustment for the ChG systems whose data are represented by the same colour.

Heavy straight lines show a general linear depen-dence obtained with taking into account all compositions of all considered ChG systems (black line) and a linear

dependence obtained in [14] (red line). In comparison with them, in Fig. 2, totally similar dependencies are represented, but obtained on the basis of the values of average bond energy E determined with the use of the algorithm from [14].
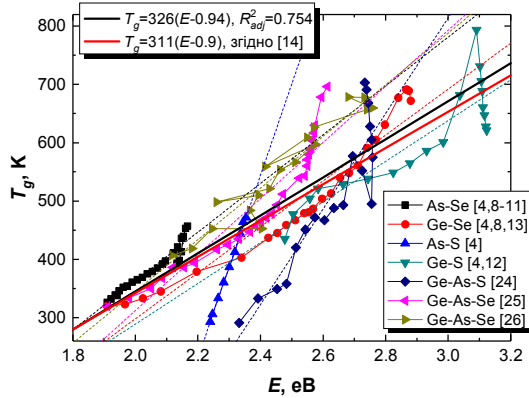

Fig. 1. Composition changes of glass transition temperature T_g with the change of average bond energy E for some ChG systems in the frame of the COCN model.
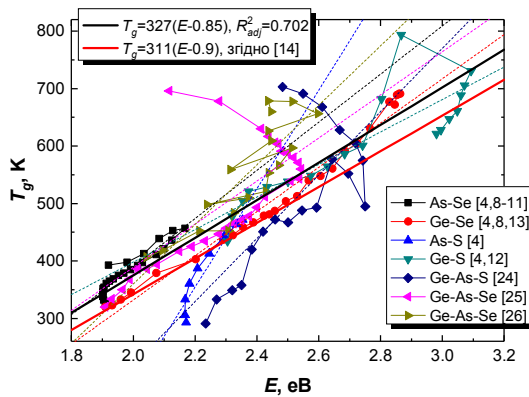

Fig. 2. Composition changes of glass transition temperature T_g with the change of average bond energy E calculated acoording to [14], for some ChG systems in the frame of the COCN model.

It is evident that there is no considerable difference between curves in Fig. 1 and Fig. 2 at the beginning of the dependences $T_g(E)$ corresponding to ChG with low Z, regardless of the algorithm used for calculating E. It allows drawing a conclusion that for these glasses the contribution of the "residual matrix" E_{rm} is insignificant. Similar results are observed for ChGs being close to stoichiometry in whose structure the heteropolar bonds prevail.

The most considerable difference can be observed for chalcogen depleted (cation-enriched) ternary ChGs Ge-As-Se/S where the nature of changing T_g with changes in E is totally different. The transition through the point of chemical stoichiometry in these ChGs is accompanied by the rapid increase in T_g with the increase in E [11,24-26]. These peculiarities are clearly

shown in Fig.1, obtained for E calculated according the algorithm proposed in this paper, but they are absent in Fig.2. As a result, the conclusion can be drawn that the use of incorrect algorithm from [14] causes observing physically impossible changes as in Fig.2, where an increase in T_g for cation-enriched ChGs Ge-As-S, $Ge_xAs_ySe_{1-x-y}$ and $Ge_xAs_xSe_{1-2x}$ is accompanied with unexpected decrease in their average bond energy E which is not conformed with equation (18).

Comparing the experimental data for ChG with equation (18) allows interpreting only the results obtained for composition changes of T_g with changing the average bond energy E calculated according to the correct algorithm shown above, that is, the results represented in Fig.1. For convenience of their treating, the values obtained as a result of mathematical adjustment of numerical parameters of the linear dependence $T_g(E)$ according to equation (18) are provided in Table 1. Besides the parameters a and b, which are directly represented in (18), root-mean-square deviation R^2_{adj} is provided in Table 1, whose value indicates the quality of applied procedure of mathematical adjustment (the closer to 1 it is, the better accuracy is obtained during the adjustment).

Table 1

Numerical parameters of linear dependence of transition temperature T_g on the average energy bonding E for some ChG systems of Ge-As-S/Se type

ChG system	a, K/eB	b, eB	R^2_{adj}
As-Se [4,8-11]	418	1.13	0.901
Ge-Se [4,8,13]	394	1.24	0.921
As-S [4]	1566	2.05	0.998
Ge-S [4,12]	349	1.17	0.774
Ge-As-S [24]	819	2.01	0.817
$Ge_xAs_ySe_{1-x-y}$ [25]	443	1.22	0.909
$Ge_xAs_xSe_{1-2x}$ [26]	481	1.35	0.878
All ChG systems [4,8-13,24-26]	326	0.94	0.754

The last conclusion is validated by the fact that the value of root-mean-square deviation at the mathematical adjustment for the case of calculating E with the use of the given algorithm ($R^2_{adj}=0.754$) is higher than at the adjustment for the case of calculation of E according to the algorithm from [14] ($R^2_{adj}=0.702$). At the same time, Table 1 shows that the quality of the mathematical adjustment increases while being used for particular ChG systems within which the limited number of different kinds of covalent bonds is realized. Therefore, the highest quality of the linear adjustment is observed for ChG systems As-S [4] ($R^2_{adj}=0.998$) and Ge-Se [4,8,13] ($R^2_{adj}=0.921$). A slope of a in equation (18) for the ChG on the basis of S is steeper that the similar parameter for ChGs containing Se.

The most unexpected result consists in the fact that, in spite of quite considerable variation of parameters *a* and *b* (Table 1) for different ChG systems, the general linear dependence $T_g(E)$ for all considered ChGs proved to be extremely close to equation obtained on the basis of erroneous calculations of *E*:

$$T_g \cong 326 \cdot (E - 0.94). \qquad (19)$$

Undoubtedly, this result is the artefact of the procedure of the choosing the ChG systems and compositions for determining such a correlation. Although different ChG show considerable variations of linear slope of *a* (Table 1), in general all of them are well clustered around the black line in Fig. 2.

4. Conclusions

The conducted critical analysis has shown that correlation between the glass transition temperature T_g and the average bond energy *E* obtained for ChG in L. Tichý & H. Tichá (J. Non-Cryst. Solids, 189, 1995) cannot be used in practice due to evident errors in the algorithm for calculating average bond energy caused by the incorrect use of averaging procedure for different components of *E*.

Having corrected this calculation algorithm with the use of 145 typical representatives of covalent-bonded network ChGs (systems of Ge-As-S/Se type), it can be shown that the real linear correlation between the glass transition temperature T_g and their bonding energy *E* (averaged regarding to the number of atoms of the formula unit of glass) calculated for the case of the COCN model can be determined by the equation $T_g \cong 326 \cdot (E - 0.94)$.

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КОРЕЛЯЦІЯ ТЕМПЕРАТУРИ РОЗМ'ЯКШЕННЯ ТА СЕРЕДНЬОЇ ЕНЕРГЕТИЧНОЇ ПОВ'ЯЗАНОСТІ СІТКОВИХ ХАЛЬКОГЕНІДНИХ СТЕКОЛ

Михайло Шпотюк, Олег Шпотюк

У статті критично проаналізовано кореляційне співвідношення між температурою розм'якшення T_g і середньою енергією зв'язків E, отримане для халькогенідних стекол в L. Tichý & H. Tichá [J. Non-Cryst. Solids, 189, 1995]. В результаті показано, що його було отримано з використанням неправильних розрахунків середньої енергетичної пов'язаності E через некоректне застосування різних процедур усереднення для різних доданків цього параметра, а тому це співвідношення не можна застосовувати на практиці. Алгоритм обчислення середньої енергетичної пов'язаності скоректовано шляхом усереднення і енергії "сіткової частини матриці" E_c (гетерополярних зв'язків), і енергії зв'язків "залишкової матриці" E_{rm} (енергії гомополярних зв'язків) на один атом формульної одиниці скла, а також врахування неможливості формування ковалентних хімічних зв'язків між катіонами різного виду. На прикладі 145 типових представників ковалентно пов'язаних сіткових халькогенідних стекол (системи типу Ge-As-S/Se) показано, що реальна лінійна кореляція між температурою розм'якшення T_g і їх енергетичною пов'язаністю E може визначатись співвідношенням

$$T_g \cong 326 \cdot (E - 0.94).$$

Mykhaylo Shpotyuk waas borned on Aug, 30, 1985 in Brody, Ukraine. His current position is Leading researcher of the Oxide Crystal Physics Laboratory of Lviv Polytechnic National University (Lviv, Ukraine). M. Shpotyuk is Doctor of Phys.-Math. Sciences (speciality 01.04.07 – Solid State Physics) since 2018. He is author and co-author of about 120 scientific papers. His scientific interests include ageing effects and induced phenomena in chalcogenide vitreous semiconductors.

Oleh Shpotyuk waas borned on Apr, 21, 1958 in Brody, Ukraine. His current positions are Head of Sector of O.G. Vlokh Institute of Physical Optics (Lviv, Ukraine), Vice-Director of the Scientific Research Company "Electron-Carat" (Lviv, Ukraine) and Professor of Jan Dlugosz University in Czestochowa (Czestochowa, Poland). O. Shpotyuk is Doctor of Phys.-Math. Sciences (speciality 01.04.07 – Solid State Physics) since 1991, Professor on "Solid State Physics" specialization since 1999. He is author and co-author of about 1000 scientific papers. His scientific interests include structure and degradation-relaxation transformations in disordered solids.