SOME REMARKS ON THE GLASS-TRANSITION TEMPERATURE IN CHALCOGENIDE GLASSES: A CORRELATION WITH THE MICROHARDNESS

RUBEN JERONIMO FREITAS[a*], K. SHIMAKAWA[b,c], AND S. KUGLER[c]
[a]*Department of Electrical and Electronic Engineering, National University of Timor Lorosa'e,Av. Cidade de Lisboa Dili, East Timor*
[b]*Department of Electric and Electronic Engineering, Gifu University, Gifu 501-1193, Japan*
[c]*Department of General and Inorganic Chemistry, University of Pardubice, 53002 Pardubice, Czech Republic*
[d]*Department of Theoretical Physics, Budapest University of Technology and Economics,H-1521 Budapest, Hungary*

The glass-transition temperature T_g is known to be related to cohesive energy (e.g., mean bond energy $\langle E \rangle$) in most binary and ternary chalcogenide glasses, while $\langle E \rangle$ is theoretically predicted parameter. It is reported here that the hardness H from the mechanical point of view, as an accessible physical parameter of cohesive energy, is shown to correlate with T_g in most chalcogenide glasses. A factor influencing T_g in chalcogenide glasses can be primary a short-range chemical-bond arrangement but not an inter-molecular interaction.

Well known empirical relation of the glass-transition temperature of $T_g \approx 2T_m/3$, where T_m is the melting temperature in glassy materials [1], suggest that T_g is related to the cohesive energy, since T_m should be closely related to bond strength. In covalent bonding materials such as most chalcogenide glasses, cohesive energy should correspond to the bond energy, since van der Waals force between layers are not strong compared with intra-layer interaction (covalent bonding). At $T \approx T_g$, glassy network is macroscopically movable due to a sharp decrease in the viscosity. The sharp decrease in the viscosity above T_g is expected to be due to collapse of glassy network in some extent, while underlying physics is still not clear.

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* Corresponding author: cubano_jr@yahoo.com

T_g is then expected to correlate with the network rigidity which should be directly related to the mean coordination number $\langle Z \rangle$, e.g., the following relation, $\ln T_g = 1.6 \langle Z \rangle + 2.3$, is known for wide class of glasses including organic materials [2].In addition to the coordination number, Tichý and Tichá (1995) suggested that the bond energy for each bond should be taken into account for overall network. Then as shown in Fig. 1, a covalent bond approach in chalcogenide glasses produces a good correlation between T_g and the overall mean bond energy $\langle E \rangle$ (= $\Sigma c_i E_i Z_i$), where c_i, E_i, and Z_i are the ith component of the atomic fraction, the bond energy, and the coordination number, respectively [3]. This model therefore contains the factors of bond arrangement (coordination number Z) and magnitude of bond strength (bond energy E). T_g is empirically given as $T_g(K) \approx 311(\langle E \rangle - 0.9)$for 186 binary and ternary chalcogenide glasses.
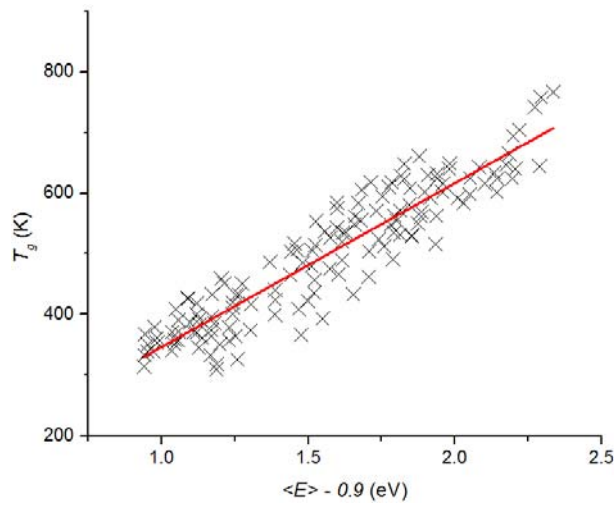

Fig. 1 Correlation between T_g (K) and $\langle E \rangle$ (eV) in chalcogenide glasses (data from ref. [3]). Solid line is the least-square fit to the data, which has been given as $T_g = 311(\langle E \rangle - 0.9)$ (see text).

It should be noted, however, that $\langle E \rangle$ or $\langle Z \rangle$ itself is not an experimentally measurable value and hence we should look for experimentally accessible physical parameters instead of $\langle E \rangle$ (or also $\langle Z \rangle$) to confirm its validity. Turn to the mechanical point of view in glasses. The mechanical hardness (microhardness) should be related microscopically to the bond strength [4, 5], we hence propose that mechanical hardness H may be a candidate of such parameter which can be closely related to the mean bond energy $\langle E \rangle$. We collected the experimental data of hardness H (Vickers hardness) from the excellent data book on chalcogenide glasses [6]. Fig. 2 shows a linear correlation between H and T_g for 190 binary and ternary chalcogenide glasses (P-Se, As-Se, As-Se-Sb, As-Se-Te, Ge-Se-Te, Ge-Se-S, P-Ge-Se, Sb-Ge-Se, Bi-Ge-Se, As-Te-I*etc*.). The correlation between H and T_g is good as well as the correlation between $\langle E \rangle$ and T_g, suggesting that H is a good physical parameter instead of *theoretically predicted* $\langle E \rangle$: H can be used as a measure of the average bond strength in chalcogenide glasses. Note that glassy components reported in T_g

vs.$\langle E \rangle$ given by Tichý and Tichá[3] are not completely the same as the present glassy systems.
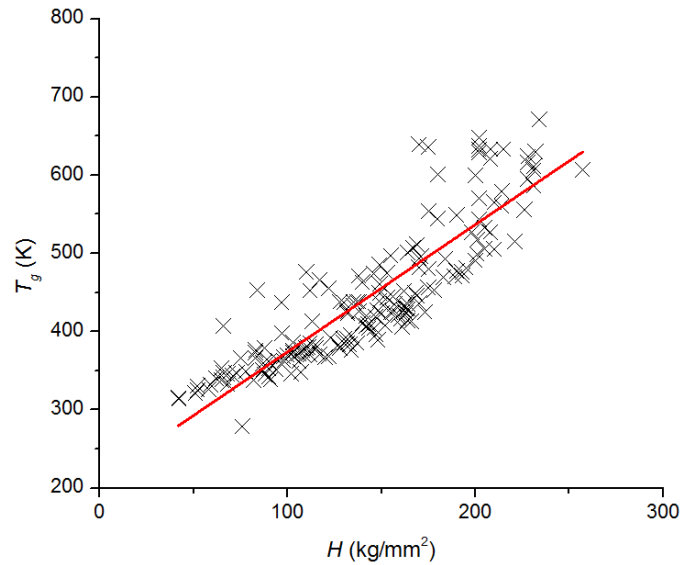

Fig. 2 Correlation between T_g (K) and H (kg/mm^2) in chalcogenide glasses. Solid line is
the least-square fit to the data, producing $T_g = 1.6H + 211$.

The microhardness of materials, on the other hand, may correlate with some other parameters, such as density ρ (g/cm^3) or atomic number density n_a (Å^{-3}), since the macroscopic mechanical parameters of materials are expected intuitively to depend on these values. Let us examine the relationships between these parameters and microhardness. Fig. 3 (a) and (b) show the relations between H vs. ρ and H vs. n_a respectively. Note again that experimental data were collected from ref. [6]. As clearly shown in figures, H does not have any correlation with ρ and n_a in most chalcogenide glasses, in contrary to an intuitive prediction.
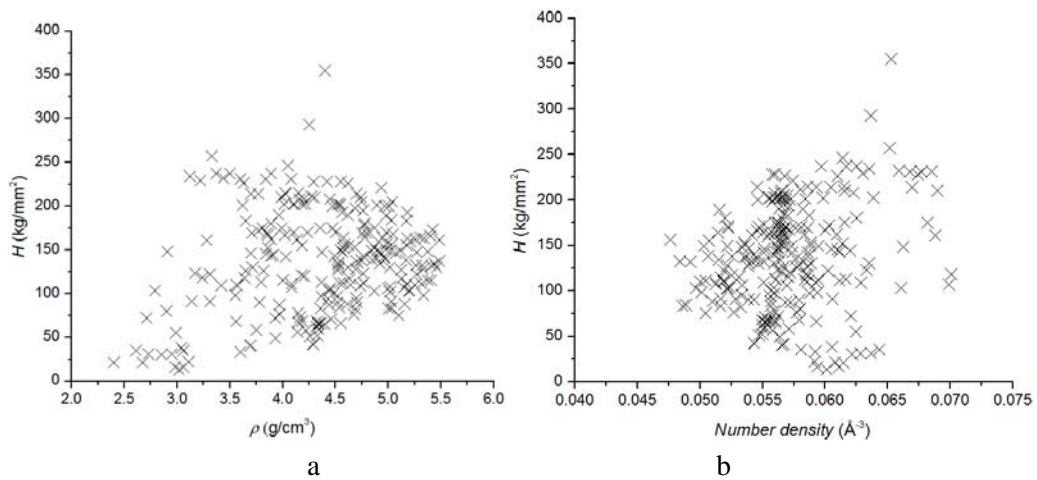

a

b

Fig 3 (a) Correlation between H (kg/mm^2) and ρ (g/cm^3) in chalcogenide glasses.
(b) Correlation between H (kg/mm^2) and n_a (Å^{-3}) in chalcogenide glasses.

We know now *H*, as a measure of average bond strength, dominates the glass transition. We also know $\langle Z \rangle$ is primary important factor for determining T_g, since it roughly gives the average number of covalent bonds. It is therefore of interest to show a correlation between $\langle Z \rangle$ and *H*, as shown in Fig. 4, which has not yet been discussed so far. *H* is weakly correlated with $\langle Z \rangle$, similar to the correlation between $\langle Z \rangle$ and T_g. This correlation indicates that the short range chemical bond arrangement is a primary important factor to determine the glass-transition temperature, since *Z* itself directly related to a short-range bond arrangement.
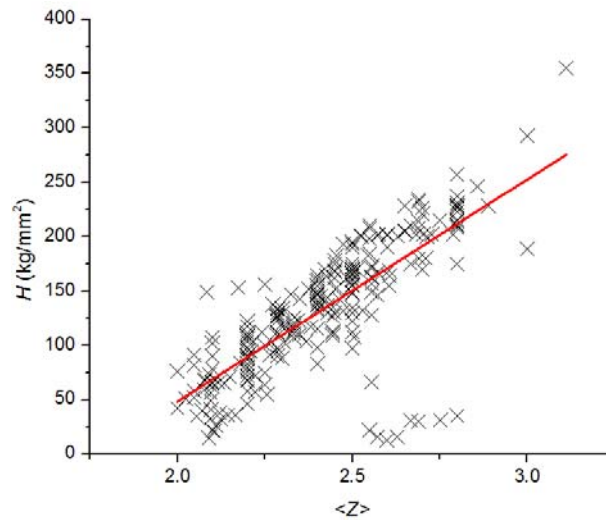

Fig. 4 Correlation between H (kg/mm²) and $\langle Z \rangle$ in chalcogenide glasses. Solid line is the least-square fit to the data, producing H = 204$\langle Z \rangle$ - 360 = 204 ($\langle Z \rangle$ - 1.76).

Finally, let us discuss the temperature-dependent viscosity. Viscosity is a macroscopic property and is dominated by cooperative process of network, which should be involved an inter-molecular interaction. The glass-transition temperature is often defined as the temperature-dependent viscosity which reaches around 10^{13} Poise (= 10^{12} Pa·s). Rapid decrease of viscosity above T_g can be attributed to a decrease of inter-molecular interaction, which can be accelerated by destroying short-range structure (bond breaking): A rapid decrease of the viscosity should accompany with intra-layer bond breaking. This may be the reason why T_g has the good relationship with $\langle E \rangle$ and hence the value of T_g depends on a feasible parameter of *H* as a measure of $\langle E \rangle$.

In summary, it is shown that the glass-transition temperature strongly correlates with the microhardness in covalent chalcogenide glasses. This result suggests that the microhardness, from the mechanical point of view, is also a measure of the magnitude of T_g. It is clear from the fact that *H* is a measure of $\langle E \rangle$ and hence a factor influencing T_g in chalcogenide glasses is primary a

short-range chemical-bond arrangement but not an inter-molecular interaction.

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