

## FRAGILE AND STRONG GLASS MELTS - A POSSIBLE STRUCTURAL EXPLANATION

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The fragile or strong character of glass forming melts is a frequently discussed subject in the last years, constituting a new manner of evidencing the existing structural differences in this kind of liquids. The propriety used, as a rule, to illustrate these differences is the viscosity variation with temperature. Strong melts follow an Arrhenius type curve and for the fragile ones a T-V-F type equation describe more satisfactory the process. Especially for oxide glass forming melts the most accepted concept is that the strong liquids have a network type structure with a uniform coordination number and high energy chemical bonds while the fragile ones have a fragmented structure with complex coordination and lower energy chemical bonds. One observes that the structural models elaborated in our laboratory reflect and explain these properties. For the fragile melts with a macro-anionic structure, the important role of dipole-dipole bonds is highlighted. Using some published data the existence of a correlation between the fragility and the basicity was evidenced. The basicity values show that the strong melts have a higher tendency to undercool in vitreous state than the fragile ones which have lower glass forming properties.

(Received August 29, 2005; accepted September 22, 2005)

*Keywords:* Melts fragility, Basicity, Dipolar bonds

### 1. Introduction

Angell formulated the idea of glass forming melts fragility and strength in some works published in the '80's, the cited one [1] being selected to focus the attention on the respective Fig. 1 where the viscosity logarithm variation is represented as a function of a reduced inverse temperature scale  $T_g/T$  using  $T_g$  as a normalizing parameter. In this coordinates the strong melts describe practically straight lines corresponding to Arrhenius type equations while the fragile ones show more complex curves. This behaviour is discussed by Angell in terms of differences in resistance against the thermal energy destructive action between a three-dimensional network structure and a more simple fragmented structure. He suggested also that the fragility may be estimated, in principle, by means of the roughness of the energy hyper surface, the coordination number consideration being useful too. Vilgis consider the energy landscape based on a Gauss type distribution adding coordination number CN as a second variable related to the random configurations and obtain some interesting results on the way of characterizing and measuring fragility [2].

It is of interest to remark that in the cited work of Angell and in the respective figure is represented the curve of  $As_2S_3$  too showing the same aspect as the oxide melts. Boolchand and co-workers [3] discussed some peculiarities of melts in the Ge-As-Se ternary. The coordination role in determining the melt behaviour was evidenced, being proposed simple formulas for a mean value calculation. One observe that, at a value of the mean coordination number  $n_c = 3.4$  the structure pass from a floppy phase to a rigid one. In these glasses one consider that the structure strength is determined by a backbone formed by tetrahedrons. The mobility is related to the presence of some

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isolated nano-phases.

A recent approach took into consideration, in order to measure the fragility, the activation energies  $Q$  (kJ/mol) according to the classical Arrhenius type relationship concerning the viscosity dependence on temperature applied to both branches of the non Arrhenius curves of fragile melts:

$$\eta = A \cdot e^{\frac{Q}{RT}} \quad (1)$$

As a measure of melts fragility the ratio between the activation energy  $Q_h$  for high viscosity branch and the activation energy  $Q_l$  for low viscosity was proposed by Doremus [4]. Using these ratios for a number of melt compositions and the basicity values calculated by means of our own basicity scale [5, 6] a correlation was evidenced between the fragility and the basicity as shown in the Fig. 1 [7].

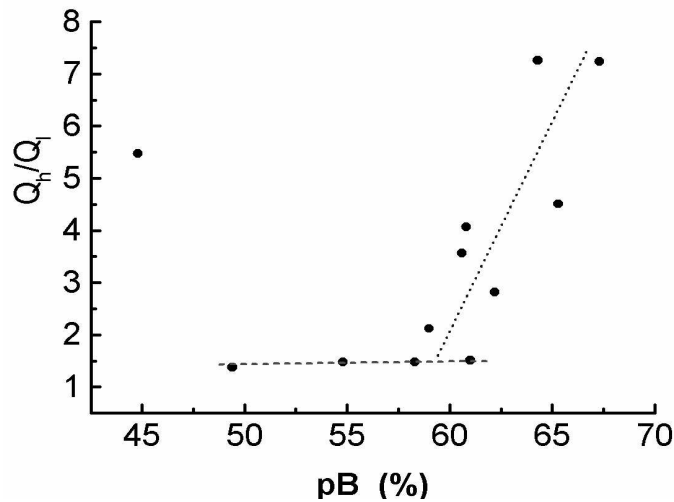


Fig. 1. The correlation between fragility and basicity.

One observe that, from the set of available data, strong melts, with ratios values close to unity, are practically placed on a strait line up to basicity of 60 %. By the basicity increase over 60 % the ratio value representing the fragility rapidly increases. In this way, by means of basicity, one deduces that strong melts belong to the glass forming compositions while the fragile ones are in the intermediary domain between formers and modifiers with basicity between 60 and 70 %.

The only exception (in Fig. 1) is the point corresponding to  $B_2O_3$  which, although has a low basicity (pB = 44.8 %) and is a recognized former, has a very high ratio of activation energies, at the level of fragile melts. It is new information, added to the known ones, confirming that the boric anhydride melt structure suffers, at the temperature increase, transformations still insufficient understood.

On the basis of this correlation a convenient way to estimate the melt fragility became available facilitating also structural interpretations.

## 2. A general image of the oxide melts structure

In the structure of oxide melts and glasses the concentration of glass former plays an important role. The three-dimensional network of  $SiO_2$  glass, for example, is fragmented by the increasing quantities of modifier oxides and at about 25 mol % it seems that the network disappears and the structure becomes macro-anionic. It is of interest to note that at approximately this modifier concentration the basicity in a binary silicate is 54 % in the presence of  $Li_2O$ , 59 % for  $Na_2O$ , 63,8 % for  $K_2O$ , 58,2 % for  $CaO$  and so on, meaning that the melt tend to become fragile.

For the three-dimensional network the Zachariasen model is considered still valid. For moderate modifier concentration, less than 25 mol %, Greaves [8] proposed the image in Fig. 2-a, representing a partly altered network. The macro-anionic structure may be imagined by means of the polymer theory which allows the polymer distribution calculation [9, 10]. In the Fig. 2-b is presented a model based on polymer distribution calculation for a sodium metasilicate melt (to simplify the drawing only three bonds of silicon were represented). The fragmented structure containing a mixture of very different aggregates is evident. This nano-heterogeneous image of the structure of melts and glasses is now agreed by the majority of specialists. The interaction energy of these structural aggregates – named sometime also clusters or molecules – depend strongly on temperature. The more abrupt slope of the viscosity curve immediately above  $T_g$  reflects, it seems, the decreasing energy of the interactions which are gradually covered by thermal energy of the system. This branch of curves extends up to temperatures corresponding approximately to 1.25 up to 1.6  $T_g$ . For example, for a hypothetical  $T_g$  temperature of 500 °C the respective temperatures are between 625 and 800 °C, that means temperature intervals of 125 up to 300 °C. These temperature intervals are known from long-time as the structural transformation domain. They can be estimated from a graph like that drawn by Angell ([1] Fig. 1) and used for estimation of the degree of fragility too.

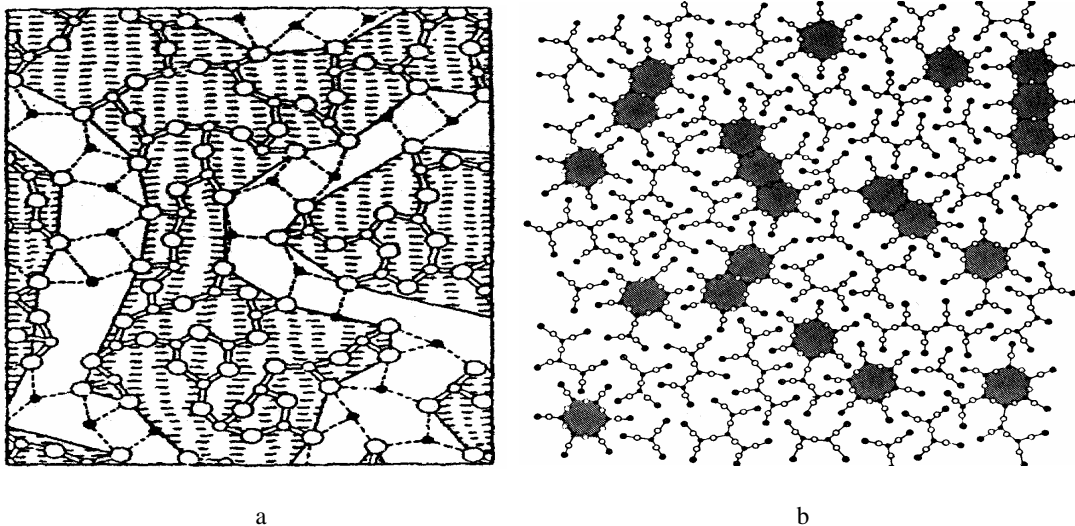


Fig. 2. The structural schemes of some silicate glasses and melts: a) strong and b) fragile.

Taking into account that this temperature interval is sometime clearly visible on recorded DTA curves as a prolonged endothermic effect after the inflexion corresponding to  $T_g$  it deserves to study the possibility to measure the structural transformation domain and in this way the fragility degree by means of DTA determinations.

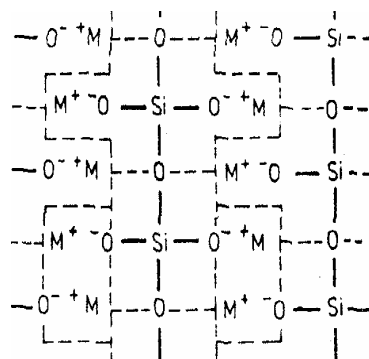


Fig. 3. Dipoles and quadrupolar bonds.

It is the place to underline that the nano-heterogeneous structure is specific for all glasses including the strong ones. Even in a unary glass of pure  $\text{SiO}_2$  were evidenced domains with dimensions in the range nano. Obviously the persistence of the network structure makes unimportant the dipoles even when present.

The problem that still remained practically unsolved is the nature of the structural transformations taking place in a glass and the respective melt above  $T_g$  till the inflexion on the curve and the lower slope branch. A convincingly solution is proposed in the next section.

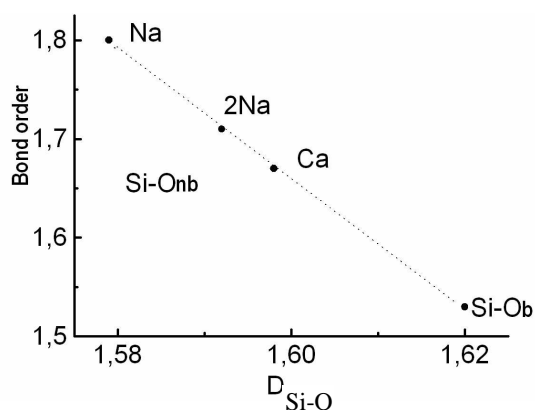


Fig. 4. Bond order of Si-O bonds in some silicates.

### 3. The role of dipole-dipole bonds in oxide melts and glasses

It seems that the first suggestion about the importance of dipoles in oxide glass structure is due to Müller (1965) in his book *Chemistry of the solid body* [11]. By means of a simple scheme like that in figure 3 he explain the presence of dipoles in structures which, as a whole, are not dipolar. Two neighbour dipoles belonging to different structural aggregates, arriving in a favourable position, may form a quadrupole that behaves as a chemical coulomb bond.

During the time some ideas and data were accumulated supporting the above presented image and allowing interesting interpretation [9, 10].

Watching the model in Fig. 2-b naturally one may admit that these structural aggregates have to interact one with other and for oxides the dipole-dipole coulomb bonds are most probable. The energy of dipole-dipole bonds depend on the partial electrical charges of the two ions, on the distances between the opposite sign charges and on the thermal energy of the system which covers more or less the bond energy.

The partial charge of the non bridging oxygen atoms is determined by the nature of the modifier ion and the number of such ions bonded to a silica tetrahedron as may be deduced from the diagram in Fig. 4 where, as examples, are represented some bond order values for  $\text{Si-O}_{\text{nb}}$  bonds in sodium and calcium silicates. A higher  $\text{Si-O}_{\text{nb}}$  bond order value means that the respective non bridging (nb) oxygen atom is closer to the Si and his electrons uses in a greater measure the d orbitals of silicon. In this way the energy of the coulomb interaction of the respective oxygen atom will be lower and the same the dipole energy. It results that in a melt, like that represented in Fig. 2-b, the energy of dipole-dipole bonds between different structural aggregates will cover a large range of values.

Under  $T_g$  these bonds are fully active, uniting firmly the structural aggregates which join in a single whole in a complex structure. So, even a macro anionic melt become a three dimensional glass with the specific properties, among others brittleness. This important role of dipolar bonds in the processes taking place at  $T_g$  in oxide glasses was supported by Eisenberg and Takahashi [12] which established a simple correlation between  $T_g$  valuea of silicates and phosphates and the magnitudes determining the dipole momentum:  $Z$ , the charge of the cation and  $a$ , the distance between bonded atoms (Fig. 5, b and c being constants).

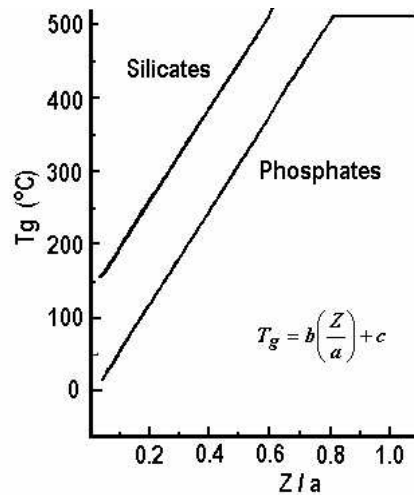


Fig. 5.  $T_g$  value dependence on charge  $Z$  and distance  $a$  between ions for silicates and phosphates.

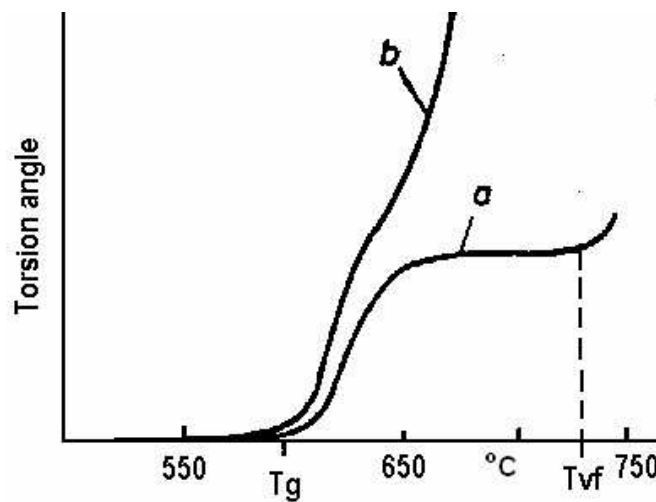


Fig. 6. High elasticity evidencing the persistence of some bonds in melt above  $T_g$ .

When the temperature increases, at  $T_g$  the thermal energy of the system surpasses the dipole-dipole bond energy and the structural aggregates begin to become free and the viscosity decreases. Because of the large spectrum of bond energies, due to the nano-heterogeneous structure of glasses, the annihilation of bonds develops step by step in a narrower or wider temperature interval, the melt showing the specific fragile behaviour.

In this way the more inclined branch of the viscosity logarithm –  $T_g/T$  curve, corresponding to the structural transformations domain, reflects the dipolar bonds yielding to the increasing thermal energy of the system.

A support of the above ideas can be found also in a work of Bartenev [13] which studied the variation of the torsion deformation of a glass rod with temperature. The results are presented in Fig. 6. The curve –a– was obtained by applying a small torsion force lower than  $1 \text{ daN}\cdot\text{cm}^{-2}$ . In such gentle conditions a so-called high elasticity was observed in a quite narrow temperature interval. This property specific for organic elastomers shows that the dipole-dipole interactions did not change abruptly at  $T_g$  but gradually, resisting to such small supplementary forces still about  $130^\circ$ . Finally the increased thermal energy covers the dipole-dipole bond energy and at the temperature indicated in Fig. 6 by  $T_{vf}$  begins the viscous flow. When the torsion force is greater than  $1 \text{ daN}\cdot\text{cm}^{-2}$

the viscous flow begins immediately above  $T_g$  because the addition of this greater force to thermal energy exceeds the rest of bonding energy of dipoles.

#### 4. Conclusions

The examination of the ideas and theories concerning the fragility of glass forming melts allowed to evidence the correlation with basicity. The fragile melts have basicities greater than 60 %. On this basis basicity constitutes a new easily accessible means for recognizing and estimation of melt fragility. Using the knowledge about basicity clearly resulted that the strong melts are better glass forming compared to the fragile ones, which have an increasing tendency, proportional to fragility, towards devitrification.

The structure of strong melts may be represented by means of the schemes imagined for oxide networks with less than 25 molar percents modifiers. For fragile melts more proper are the schemes of the macro-anionic type.

The nano-heterogeneous structure of glasses and melts and the inevitable interactions between structural aggregates impose the conclusion that the temperature interval of  $1.25 - 1.6 T_g$  corresponding to the more inclined branch of the viscosity logarithm –  $T_g / T$  curve represents the so-called structural transformation domain and may characterize the fragility. This temperature interval may be determined by means of viscosity measurements and, possibly, by means of DTA.

Some arguments accumulated during the time and supporting the presence and important role of the dipole-dipole and ion-dipole bonds in oxide glasses and melts are presented. Considering this type of coulomb interactions between structural aggregates, a convincingly explanation for the fragility of oxide melts was proposed, allowing also the understanding of the structural transformations taking place above  $T_g$ .

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