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Fragility percentage evaluation for glass forming melts

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The dependence of the viscosity on temperature for glass forming melts separates them into two categories: fragile and strong. We propose an intuitive method for quantitative evaluation of the glass forming melts fragility by a structural parameter – fragility percentage pF which allows the comparison of the glass melts without considering their particular chemical composition. A strong correlation between fragility percentage and the main number of non-bridged oxygen (O_{nb}) was established. The study is also related to a numerical application of the proposed indicator made for glass with different chemical compositions compared with the base oxide system Na_2O-SiO_2. The greater the basicity of the glasses the more fragile character of the glass forming melts is observed.

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1. Introduction

Structural peculiarities of the glass forming melts determine their properties, specifically the viscosity values a parameter which is directly related to their fragility. It is known that the breakage of the vitreous materials is fragile type. In the field of glass chemistry and technology, *fragility* can be defined as the material property of instant self deterioration under a force higher than its resistance limit. Balta [1] discuused the strong and fragile melts and gave a structural explanation. More recently, from another point of view, Angell [2] has defined two edge groups of liquids (glass melts): fragile and strong where the "fragile" attribute is associated to those structural particularities of vitreous systems, which provide particular temperature dependence of the transport properties. To be specific, *strong* vitreous melts has a dynamic viscosity η which obeys an Arrhenius law:

$$\eta = \mathrm{M} \cdot \exp(\mathrm{N}/\mathrm{T}) \tag{1}$$

where *M* and *N* are specific constants of a particular melt (liquid). In contrast to the previous category, *fragile* glass forming melts, at the limit, follow the Vogel-Fulcher - Tammann (VFT) law:

$$\eta = \mathrm{A} \cdot \exp\left[\mathrm{B}/(\mathrm{T}-\mathrm{T}_0)\right] \tag{2}$$

with, *A, B,* and T_0 material coefficients.

2. Experimental

Usually, Eq. 1 and 2are plotted as logη vs. T_g/T with T_g the glass transition temperature of the vitreous system ($T \geq T_g$). In these co-ordinates the Eq. 1 is a straight line whereas Eq. 2 yields a curve which deviates from linearity proportionally to the fragile character of the vitreous system. Such a dependence of viscosity on the reciprocal temperature T_g/T was presented by Rao [3] for several oxide glasses of unary (SiO_2, GeO_2) and binary ($Na_2O.2SiO_2$) type as well as for non-oxide type glasses represented by chalcogenides (As_2O_3), halogenides ($ZnCl_2$), and, respectively, hydrogenides. The plot revealed the almost ideal *strong* character of SiO_2 melt while other melts display a more or less pronounced *fragile* character. This difference in the behavior can be explained only relatively to the structural particularities of each analyzed glass forming system.

The *T*-dependence of the viscosity, respectively, their *fragile* or *strong* character at temperatures greater than the glass transition temperature T_g. is related to the fact that the glass forming systems have distributed values either for the coordination numbers of the constituent atoms or for the free energy [1-3].

At atomic scale, the structure of solids can be described either as a series of stereo-chemical characteristics (inter-nuclear distances, angles between bonding orbital, co-ordination numbers) or by the nature and the intensity of the interactions between the constitutive ions. For the ideal crystals, all the structural parameters have constant values in the whole volume of the solids. In the case of real crystals there is very small dispersion of these parameters around the average values. The vitreous systems involve a more or less pronounced disorder degree related to the compositionally analog crystals. Consequently, it results a much greater dispersion of the values of different stereo-chemical parameters.

For many vitreous systems, the nature of the interactions between different structural entities is different being of dominant covalent and /or ionic type and/or dipole-dipole type. As an example, in alkali-silicate glasses we can find simultaneously:

- Preponderant covalent bonds between the Si atoms and the related bridged oxygen O_p;

- Strong ionic bonds between the alkaline ions and the non bridged oxygen, O_{np}, ($\equiv$ Si – O_{np} …Na);

- Dipole – dipole type bonds resulting from the interaction of some dipoles – O_{np}… Na type;

For the vitreous systems, all structural particularities cause:

- A higher energetic content compared with;

- An energetic profile much more irregular both at the surface and in the bulk relative to crystalline solids.

Correspondingly, correlations between chemical compositions, structure, topological particularities occur also for the chalcogenide vitreous systems. In accordance with the concept of *rigidity percolation,* one considers that the glass forming ability as well as several other glass properties could be determined by the average co-ordination number [5], CN_m, from the relation:

$$CN = \sum n_i X_i \tag{3}$$

where n_i is the co-ordination number of the component *i* and X_i is the atomic fraction of the component *i*.

In 1979 Philips [5] inserted his *constraint theory* which suggests that the ability to form glasses in chalcogenide binary systems is conditioned by a value of 2.4 of CN_m. E.g., for Ge_xS_{1-x} type compositions, this condition is granted for x = 0.2 which was further experimentally confirmed. [6].The role of the average number of co-ordination is emphasized in the case of the chalcogenide glass melts behavior. For compositions with CN_m = 3.4 from Ge-As-Se system, a transformation from melts to a rigid phase occurred. [7].

In this these circumstances if we conclude that the average number of co-ordination is an important structural parameter for the chalcogenide vitreous systems, it is expected that NC_m influence several of their properties. Among the properties which depend on the average co-ordination number, we distinguish the temperature of glass transition T_g, which is an important parameter associated to weight transfer phenomena in the glass forming melts.

So, for the chalcogenide glasses $(GeS_2)_x$ $(As_2Se)_{1-x}$, Tanaka [8] proposes an estimative relation for T_g evaluation:

$$T_g = \exp\left(1.6CN_m + 2.3\right) \tag{4}$$

Where the CN_m value for the glass $Ge_{x/s}As_{2(1-x)/s}S_{3(1-x)/s}Se2_{x/st}$ is:

$$CN_m = 4\ (3\text{-}x)\ /\ s \tag{5}$$

$$s = 5 - 2x \tag{6}$$

here, CN(Ge) = 4; CN(As) = 3; CN(S) = CN(Se) = 2 are the co-ordination numbers for the constituent atoms.

Consequently, it is necessary the quantitative evaluation of the fragile character of a glass forming melt correlated to their structural particularities.

Actually, several theories and evaluation methods for the fragile / strong character of a glass forming melt are available [2-4, 9-11]. Accordingly, different values obtained for the fragility of glass forming systems could be used to compare glasses and analyze them only in accordance with a related methodology. Therefore, the values provided by different approaches can not be correlated as long as they are related to diverse scales.

Consequently, it is important to define a measure general use for the evaluation of the fragility in the case of a glass forming melts. The present paper proposes the **fragility percentage pF** as indicator for the evaluation of the fragility of glasses.

The new quantity, the **fragility percentage pF,** is zero for the strong systems (pF = 0 %) and, respectively, pF = 100 % for the ideal fragile systems for $T \geq T_g$.

3. Results and discussions

In order to define the **fragility percentage pF**, we start rewriting the Eq's. 1 and 2 as a function of
$\theta = Tg/T$:

$$\lg \eta_1(\theta) = \lg M + 0.434 \cdot N \cdot \theta / T_g \tag{7}$$

$$\lg \eta_2(\theta) = \lg A + 0.434 \cdot \left(\frac{B \cdot \theta}{T_g}\right) \Big/ \left(1 - \frac{T_0 \cdot \theta}{T_g}\right) \tag{8}$$

At high temperatures $T >> T_g$, $\theta \to 0$ for the glass forming melts, and, despite their strong or fragile character according to the Eq's (7) and (8) it results $\eta_1(0) = \eta_2(0)$ i.e., M = A.

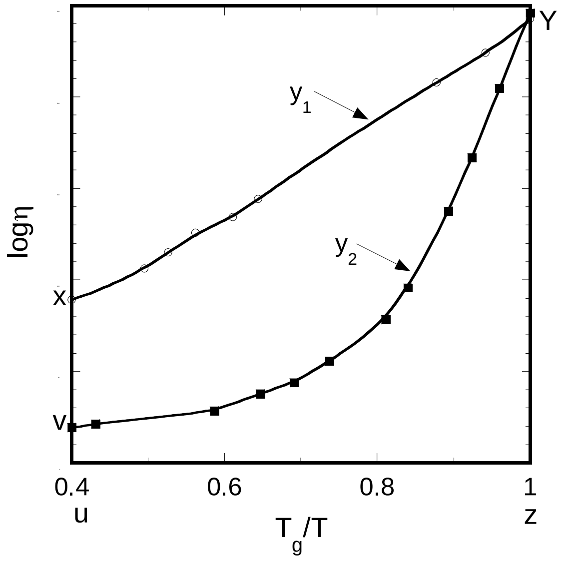

Fig. 1. Viscosity versus reciprocal temperature for two types of vitreous melts .

Because at the temperature of the glass transition T_g all the glasses have the same viscosity, for $T = T_g$, it results $\theta = 1$ and $\lg \eta_1 = \lg \eta_2$. So, from Eq. (7) and (8), with M = A ($\theta = 1$) one can write:

$$N = B / \left(1 - \frac{T_0}{T_g}\right) \tag{9}$$

Considering the relation (9), the Eq. (7) could be rewritten as follows:

$$\lg \eta_1(\theta) = \lg A + 0.434\left(\frac{B \cdot \theta}{T_g}\right) / \left(1 - \frac{T_0}{T_g}\right) \tag{10}$$

Inserting the new variables:

$$\lg \eta_1(\theta) = y_1(\theta)\ ; \qquad \lg A = a\ ;$$

$$0.434\left(\frac{B}{T_g}\right) / \left(1 - \frac{T_0}{T_g}\right) = b$$

$$\lg \eta_2(\theta) = y_2(\theta)\ ; \quad 0.434\frac{B}{T_g} = c\ ; \qquad -\frac{T_0}{T_g} = d$$

In accordance with the diagram presented in Fig. 1 obtained from Ref. 3, the fragile character of a glass forming melt for θ = T_g/T can be evaluated trough the difference $y_1(\theta) - y_2(\theta)$. When θ values are in the range $[\theta_0, 1]$, ***the fragility F*** can be calculated from the relation:

$$F = \int_{\theta_0}^{1} [y_1(\theta) - y_2(\theta)] d\theta \tag{11}$$

and ***the fragility percentage pF*** can be expressed:

$$pF = \frac{F}{\int_{\theta_0}^{1} y_1(\theta) d\theta} \cdot 100 = \left(1 - \frac{\int_{\theta_0}^{1} y_2(\theta) d\theta}{\int_{\theta_0}^{1} y_1(\theta) d\theta}\right) \cdot 100 \tag{12}$$

Considering the above used notations, ***the fragility percentage pF,*** can be successively expressed as:

$$pF = \frac{a(1-\theta_0) + 0.5 \cdot b(1-\theta_0^2)}{\left(a + \frac{c}{d}\right)(1-\theta_0) - \frac{c}{d^2} \cdot \ln\frac{1+d}{1+d\cdot\theta_0}} \cdot 100, [\%] \tag{13}$$

This for $\theta_0 = 0$ becomes:

$$pF = \frac{a + 0.5 \cdot b}{a + \frac{c}{d} - \frac{c}{d^2} \cdot \ln(1+d)} \cdot 100, [\%] \tag{14}$$

Taking into account the relation VFT (Eq. 2) and the values of A, B, T_0 and, respectively T_g, the Eq. (13) and (14) were used for the evaluation of the fragility percentage.

Application

Based on the experimental data, the viscosity dependence on temperature for a series of glasses from the *Na_2O – SiO_2* system was analyzed. It allowed the calculation of the values A, B, T_0 from the VFT relationship, and, respectively, the temperature of glass transition T_g [12].

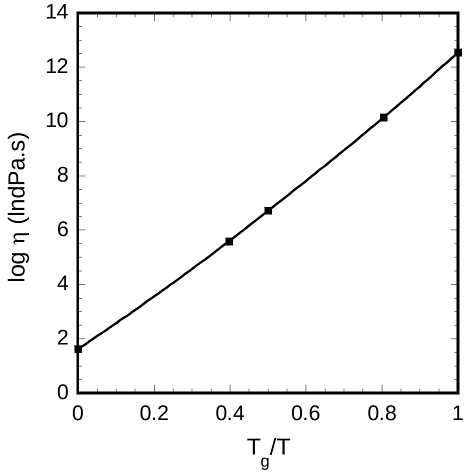

Fig. 2. Viscosity vs. reciprocal temperature for the SiO_2 glass.

The study of the lg η vs. θ dependence of four silicate glasses: SiO_2, $Na_2O.2SiO_2$, 44 $Na_2O.56$ SiO_2 and Na_2O. SiO_2 were proposed. Using the relation (13) with $\theta_0 = 0.5$ the fragility percentage pF was calculated. In the Figures 2 and 3 are presented the plots of viscosity vs. reciprocal temperature for two glasses.

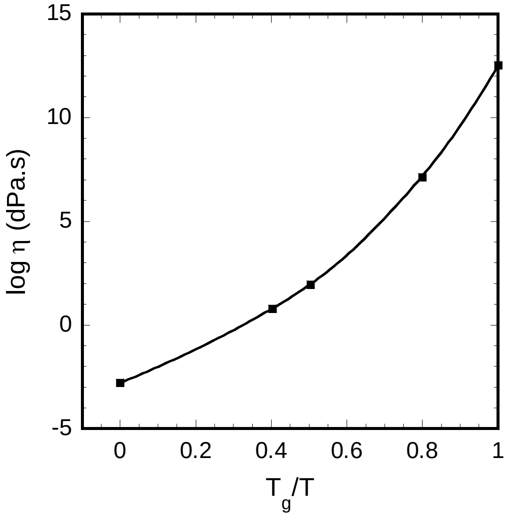

Fig. 3. Viscosity vs. reciprocal temperature for $Na_2O.2$ SiO_2 glasses.

The fragility percentage pF function of the oxide composition for the glasses of the system Na_2O – SiO_2 is presented in Fig. 4.

The Fig. 4 shows that the fragility percentage pF reaches the highest values for the glass forming melts in the system Na_2O – SiO_2 when the alkaline oxides percentage is high. The explanation consists in the fact that the same variation occurs in the basicity of glasses with the number of non-bridged oxygens O_{np} which are separated by a silicon atom. The final effect is an increase of the number of O_{np} type dipole-dipole interactions.

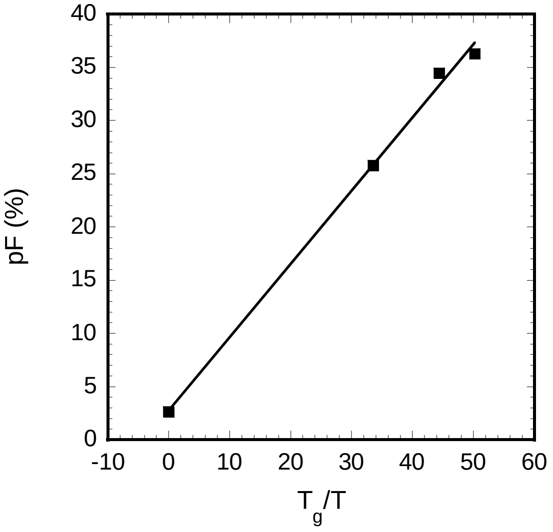

Fig. 4.The fragility percentage pF vs. oxide composition for several glasses from the $Na_2O – SiO_2$ system

5. Conclusions

This paper proposes a measure –***the fragility percentage pF*** – which estimates the degree of the fragile character of a glass forming melt. This indicator is defined related to a series of material coefficients, which are involved in the evaluation of the viscosity of the glasses and glass transition temperature, using Arrhenius, respectively, Vogel – Fulcher - Tammann laws.

Apart from other evaluation methods of the fragility, the new proposed indicator offers the advantage to dispose any glass melt on a scale from 0 to 100 (%) and consequently to make possible a direct comparison of glasses without considering their chemical compositions. This approach facilitates the obtaining and the understanding of the dependences between certain properties and the glass forming melts fragility.

Finally, the correlation between pF and the chemical composition for a number of glasses from the system Na_2O-SiO_2 was established.

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