RELATIONSHIP BETWEEN GLASS-FORMING ABILITY AND GLASS STABILITY

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All materials are able to vitrify if the cooling rates used to solidify their melts are fast enough to avoid the occurrence of a detectable crystallized fraction, usually assumed to be between 10^{-2} to 10^{-6}. The cooling rate to produce that minimum crystallized fraction is denominated *critical cooling rate*, R_c. However, R_c is difficult to be measured.

We observed recently that the Hrubÿ parameter of glass stability (K_{gl}), which is easy to measure, could be used to estimate the vitrification ability of glass forming liquids [1]. In that research, the *calculated* critical cooling rates (R_c') of four glasses were compared with K_{gl}, showing a correlation. As only four systems were analyzed in [1], in this research we decided to test other three glasses to generalize or not the findings of [1]. In addition, we felt that experimental (rather than calculated) R_c should be used in the present article.

We modified a DSC method proposed by Colmenero e Barandiarán [2] and *determined* the critical cooling rates of seven model glasses. We used almost stoichiometric compositions: $Li_2O.2SiO_2$ (LS_2), $Na_2O.2CaO.3SiO_2$ (NC_2S_3), $2Na_2O.CaO.3SiO_2$ (N_2CS_3), $BaO.2SiO_2$ (BS_2), $Li_2.2SiO_2.OH$ (LS_2OH), $2BaO.TiO_2.2SiO_2$ (B_2TS_2) and $0.44Na_2O.0.56SiO_2$ (NS). We performed the experiments in two steps. In the first, we heated monolithic pieces of these different glasses in Pt, Alumina or graphite crucibles (at the same heating rate) to estimate the Hrubÿ parameter. Then, we melted and cooled the same samples using variable cooling rates (from 1 to 50 °C/min) rates and used their crystallization temperatures to estimate R_c. An effect of the crucible material on the crystallization temperatures of these glasses was detected. We confirm the relationship between R_c and K_{gl} proposed in [1] and discuss the relevance of the our findings to the vitrification of reluctant glass-forming systems, such as metallic and fluoride glasses.

In the following sections we briefly describe and discuss the relevant theory, the experimental methods used and the results.

Several methods have been proposed to calculate R_c. One of the simplest is the so-called *nose method*, which refers to the nose of a TTT (time-temperature-transformation) diagram. According to this method, there is a corresponding time t_n for the temperature T_n of the "nose" of TTT diagrams. Thus, the critical cooling rate for glass formation is given by

$$R_c = \frac{T_m - T_n}{t_n} \qquad (1.1)$$

where T_m is the melting point of the crystal phase or liquidus temperature.

The R_c determined by the *nose method* is less than an order of magnitude larger than the real R_c. Thus one can use the nose method to *estimate* critical cooling rates and to compare the vitrification ability of different materials [1].

Colmenero & Barandiarán (CB) [2] suggested another experimental method to determine R_c. According to their ideas, the cooling rates are proportional to $(\Delta T_c)^{-2}$, which can be measured by DSC (Differential Scanning Calorimetry). The expression proposed in [2] is:

$$LnR = A - \frac{B}{(\Delta T_c)^2} \qquad (1.2)$$

where $\Delta T_c = T_m - T_c$; T_c is the crystallization temperature on cooling. The value of the constant A can be determined from the intercept of the straight line with the y-axis (Ln R), and B can

be obtained from the curve slope. When ΔT_c increases to infinity, no crystallization occurs, leading to:

$$Ln\ R = A \qquad (1.3)$$

Therefore, as the value of A is now known, it is possible to calculate R_c from equation (1.3):

$$R_c = exp\ (A) \qquad (1.4)$$

Hrubÿ proposed that a different parameter, K_{gl} obtained by Differential Thermal Analysis (DTA) or DSC, indicate the *glass stability* against crystallization on heating [1]. The Hrubÿ parameter is defined by:

$$K_{gl} = \frac{T_c - T_g}{T_m - T_c} \qquad (1.5)$$

where T_c, T_g and T_m are the crystallization temperature (on heating), glass transition and melting temperatures, respectively. According to Hrubÿ, the higher the value of K_{gl} of a certain glass, the higher its stability against crystallization and, *supposedly* the higher its vitrification ability [3].

We carried out several experiments (Netzsch DSC equipment, with a controller model TASC 414/3, cell model DSC 404) using the seven glass samples mentioned above. The first four glasses were prepared at the Vitreous Materials Laboratory - LaMaV/DEMa-Ufscar, the following two were synthesized at the Institute of Silicate Chemistry in St Petersburg, Russia and B_2TS_2 was made at the Otto-Schott Institute in Jena, Germany.

Monolithic glass pieces, weighting approximately 10 to 20 mg were placed in a Pt crucible. We used the same heating rate (20 K/min) for all the samples but varied the cooling rates to embrace the theoretical values of R_c previously calculated by Cabral et al [1].

To test the reproducibility of the crystallization temperatures, we made the following modification in the CB method. We carried out at least three cooling experiments for each different cooling rate. In cases where more than one peak appeared in the cooling trace of a given DSC run, only the peak at the highest T was considered in the calculations. We made this choice because at temperatures smaller than the first peak, crystals already exist in the sample. Then we repeated the experiments, at least three times for each cooling rate, and took the lowest T_c peak to privilege volume (homogeneous) crystallization rather than surface crystallization.

We performed several experiments for each glass and found different values for K_{gl}'s and R_c. As an example, Fig.1 displays the data obtained in one experiment with NC_2S_3. Thus, according to the equation obtained from Fig. 1 and Eq. (1.4): $R_c \sim 12$ K/s.

We adopted the same procedure for the other samples and plotted Ln (R_c) x K_{gl} for all the glasses. Figure 2 shows that the higher the K_{gl}, the smaller the Rc!

Similar experiments were carried out with LS_2 glass in Pt, Al_2O_3 and graphite crucibles. Their crystallization temperatures in the three types of crucibles were significantly different. Pt and Al_2O_3 influence both the crystallization temperatures and Rc of LS_2 (and probably of other systems), increasing and decreasing its R_c, respectively. This can be explained by the fact the Pt is a powerful nucleating agent for LS_2 glasses, thus inducing heterogeneous nucleation at the crucible walls [5]. On the other hand, it is well known that alumina increases the glass viscosity thus decreasing the nucleation rates [6].

Despite this drawback, the overall results of this research indicate that the K_{gl} parameter, which is easy to measure, can be used to compare the relative vitrification tendency of good glass-forming systems. We hope that the method can also be applied to reluctant glass formers, such as metallic and fluoride glasses. In this case, for instance, variations of K_{gl} with addition of certain compounds to the base glass could be used to optimize glass-forming compositions.

Preliminary Conclusions

The experimental R_c obtained by the CB technique, modified in this work to privilege bulk nucleation, are consistent with experimental observations on melting and quenching the glasses.

The R_c obtained with Pt crucibles were one order of magnitude larger than those predicted from TTT curves. Despite this drawback, the CB method can be used to estimate the vitrification tendency and to compare different materials.

The correlation between the Hrubÿ parameter of glass stability and the glass-forming tendency was confirmed.

Acknowledgments

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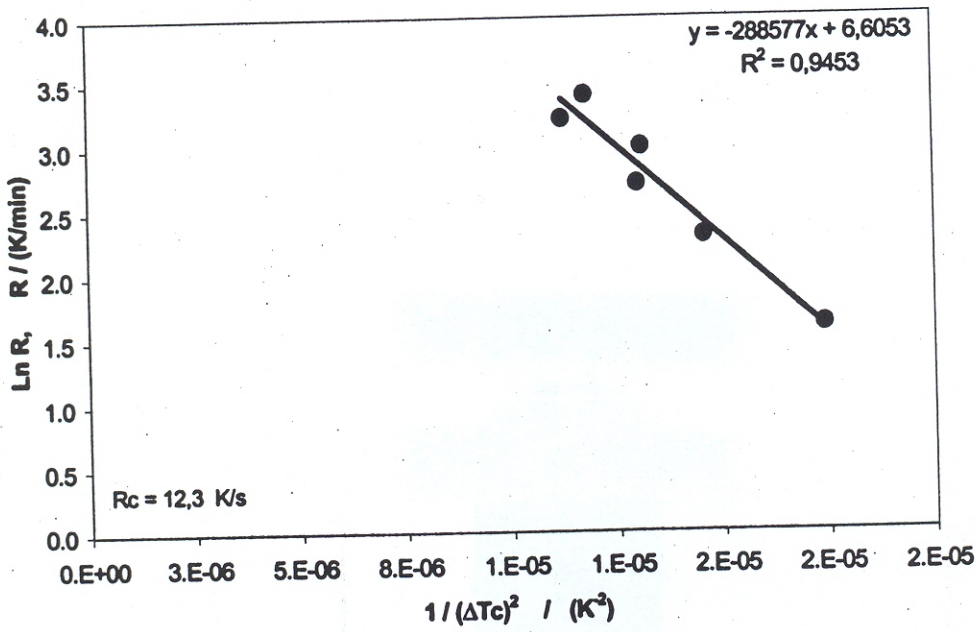Figure 1. Ln R x $1/(\Delta T)^2$ for the NC_2S_3 glass. The straight-line equation, its R^2 and the values of R_c are shown.
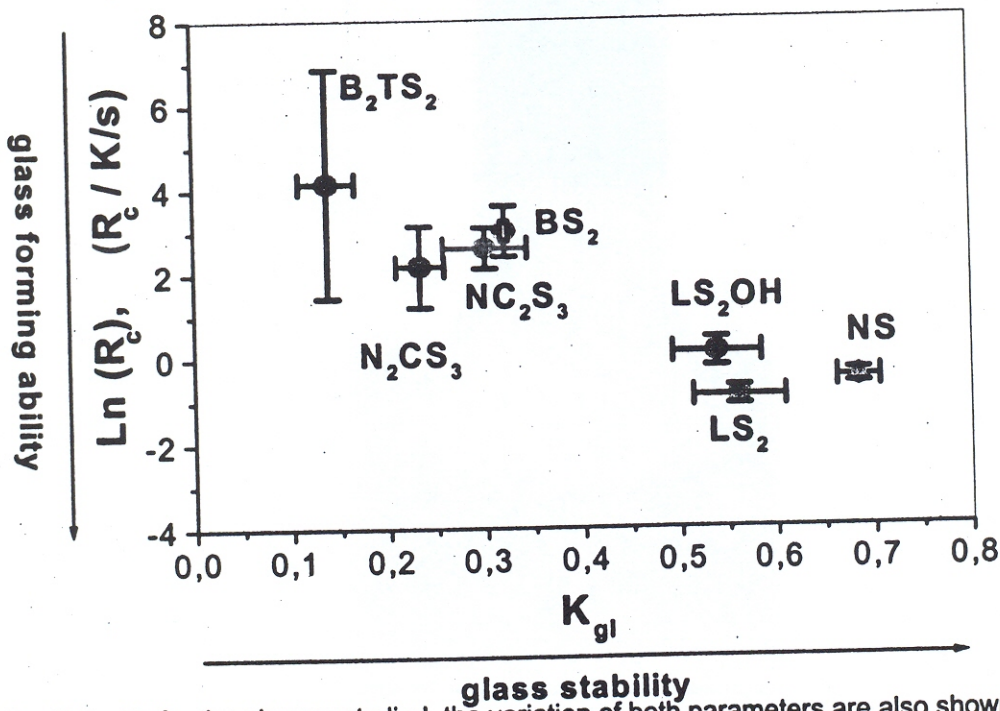

Figure 2. Ln (R_c) x K_{gl} for the glasses studied, the variation of both parameters are also shown.