Glass-forming ability versus stability of silicate glasses. I. Experimental test

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Abstract

We recently proposed that the Hrubÿ parameter of glass stability (K_H) could be used to estimate the vitrification ability of glasses that nucleate internally. In that research, we used calculated critical cooling rates (q_{cr}) for four glasses. In this article, we report on our measurements of the critical cooling rates of seven glasses: $Li_2O \cdot 2SiO_2$, $Na_2O \cdot 2CaO \cdot 3SiO_2$, $2Na_2O \cdot CaO \cdot 3SiO_2$, $BaO \cdot 2SiO_2$, $Li_2O \cdot 2SiO_2 \cdot OH$, $2BaO \cdot TiO_2 \cdot 2SiO_2$ and $0.44Na_2O \cdot 0.56SiO_2$. We modified and used a method put forward by Colmenero and Barandiarán (CB) to estimate the q_{cr}. The experiments were accomplished in two steps. In the first, monolithic pieces of each glass, obtained by splat cooling the melts, were heated in a Pt crucible, at the same heating rate, to estimate the glass transition, crystallization and melting temperatures. We then calculated the Hrubÿ parameter, K_H, based on these quantities. In the second step, the same samples were melted, then cooled at different rates and the crystallization temperatures observed were used to estimate q_{cr}. In another set of tests, we used Al_2O_3 and graphite crucibles, repeating the same procedures for the LS_2 glass. The effect of the crucible's material (Pt, C and Al_2O_3) on the crystallization temperatures is discussed. A relationship between q_{cr} and K_H is experimentally demonstrated.
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1. Introduction

All materials are vitrifiable if the cooling rates used to solidify their melts are fast enough to prevent the occurrence of a detectable fraction of crystals, usually assumed to lie between 10^{-2} and 10^{-6}. The cooling rate to produce that minimum crystallized fraction is denominated the *critical cooling rate*, q_{cr}. However, it is quite difficult to accurately measure the q_{cr}.

We recently observed that the Hrubÿ parameter (K_H), which easily measures glass stability (GS) against devitrification on heating, can be used to estimate the glass-forming ability (GFA) on cooling [1]. In that research, the *calculated* critical cooling rates (q'_{cr}) of four glasses were compared with K_H, demonstrating a correlation. However,

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our results contradicted Weinberg's [2] suggestion, which affirmed that, although GFA and GS are related concepts, they are ill-related quantities. Additionally, because we had analyzed only four systems in Ref. [1], in this research we test another three glasses to generalize (or not) our previous findings. Furthermore, we use an experimental rather than calculated q_{cr}.

1.1. Literature review

Twenty years ago, Colmenero and Barandiarán [3] proposed an experimental method to measure critical cooling rates using thermal analysis techniques (DSC or DTA). This method will be dubbed the CB method. As far as we know, only a few researchers have tested this method to estimate q_{cr}. We will briefly review some of them in the following paragraphs.

Wichard and Day [4] determined the critical cooling rates for five compositions of the Ga_2O_3–CaO system. Using a Pt–10% Rh thermocouple, they determined q_{cr} by repeated cooling and heating experiments. Each composition was melted between 150 and 250 °C above its respective *liquidus* and cooled at least 30 times at various rates. As they expected, eutectic compositions displayed a greater tendency to vitrify.

Another interesting study was conducted by Huang et al. [5]. Using a glass of nominal composition $40Li_2O$–$60SiO_2$ mole%, they showed that q_{cr} increases with increasing Pt and Au additions, but Pt has a stronger effect than Au. They used two methods for q_{cr} measurements, the first being the one used by Wichard and Day [4], and the second the one proposed by Colmenero and Barandiarán [3]. An excellent agreement was found between these values, even when different amounts of Pt and Au were used.

Finally, Ray and Day [6] measured the critical cooling rates for five compositions of the BaO–TiO_2–SiO_2 system, suggesting that the tendency for glass formation increases with increasing silica content, as expected.

In the present paper, we report on our *modification* of the CB method [3] and determination of the critical cooling rates of seven 'model' glasses (that show internal nucleation) having almost

stoichiometric compositions: $Li_2O \cdot 2SiO_2$ (LS_2), $Na_2O \cdot 2CaO \cdot 3SiO_2$ (NC_2S_3), $2Na_2O \cdot CaO \cdot 3SiO_2$ (N_2CS_3), $BaO \cdot 2SiO_2$ (BS_2), $Li_2O \cdot 2SiO_2$ with 0.2% mole OH (LS_2OH), $2BaO \cdot TiO_2 \cdot 2SiO_2$ (B_2TS_2) and $0.44Na_2O \cdot 0.56SiO_2$ (NS).

Our experiments were performed in two steps. In the first, monolithic pieces of each glass were heated in Pt, alumina or graphite crucibles (at the same heating rate) to estimate the Hrubÿ parameter and test its sensitivity to the crucible material. Then, the same samples were melted and cooled at variable cooling rates (from 1 to 50 °C/min) and their crystallization temperatures on cooling used to estimate q_{cr} by the modified CB method. An important effect of the crucible material on the crystallization temperatures of these glasses was detected. We confirm the relationship between q_{cr} and K_H proposed in Ref. [1] and discuss the relevance of these findings to the vitrification of reluctant glass-forming systems.

The following sections describe and discuss the relevant theory, the experimental methods used and the results of this research.

2. Theory

2.1. Methods to determine q_{cr}

Several methods have been proposed to calculate critical cooling rates, q_{cr}. 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, q_{cr}^n, is given by

$$q_{cr}^n = \frac{T_m - T_n}{t_n},\tag{1}$$

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

The q_{cr} determined by the *nose method* is typically less than an order of magnitude greater than the real q_{cr} [7]. Thus, the nose method can be used to *estimate* critical cooling rates and to compare the vitrifiability of different materials [1].

Colmenero and Barandiarán (CB) [3] suggested another experimental method to determine q_{cr}. According to these authors, the cooling rates, which can be measured by differential scanning calorimetry (DSC), are proportional to $(\Delta T_c^c)^{-2}$. The expression proposed in [3] is

$$\ln q = A - \frac{B}{(\Delta T_c^c)^2}, \tag{2}$$

where $\Delta T_c^c = T_m - T_c^c$, T_c^c is the peak crystallization temperature on cooling the sample at a cooling rate q. By varying the cooling rate and plotting $\ln(q)$ versus $1/(\Delta T_c^c)^2$, if the equation is correct, one should obtain a straight line. The constant A can be determined from the intercept of the straight line and B can be obtained from the curve slope. According to [3], when ΔT_c^c increases to infinity, no crystallization occurs, leading to

$$\ln q_{cr} = A. \tag{3a}$$

Therefore, as the value of A is already known, it is possible to calculate q_{cr} from Eq. (3a).

One should be aware, however, that ΔT_c^c never tends to infinity because it can only vary between T_m and zero. Therefore, we propose a more realistic expression for q_{cr}, hereinafter called q_{cr}^*, given by the following equation:

$$\ln q_{cr}^* = A - \frac{B}{T_m^2}. \tag{3b}$$

2.2. The Hrubÿ parameter of glass stability

Hrubÿ proposed that a parameter, K_H, obtained by differential thermal analysis (DTA) or DSC, indicates *glass stability* against crystallization on heating [8]. The Hrubÿ parameter is defined by

$$K_H = \frac{T_c^h - T_g}{T_m^* - T_c^h}, \tag{4}$$

where T_c^h, T_g and T_m^* are the onset crystallization temperature (on heating), glass transition and melting temperatures estimated by DSC, respectively. According to Hrubÿ, the higher the value of K_H of a certain glass, the higher its stability against crystallization on heating and, *presumably*, the higher its vitrifiability on cooling [8].

3. Experimental procedures

We carried out several DSC experiments using samples of seven glasses. The LS_2, NC_2S_3, N_2CS_3 and BS_2 glasses were prepared at the Vitreous Materials Laboratory – LaMaV/DEMa-UFSCar, the other two (LS_2OH and NS) were synthesized at the Institute of Silicate Chemistry in St Petersburg, Russia and the B_2TS_2 glass was produced at the Otto-Schott Institute in Jena, Germany. These glasses were melted in Pt crucibles at temperatures approximately 50 °C above the respective melting points of the isochemical crystals for a few hours, homogenized and quenched by pressing the liquid between two steel plates.

Monolithic glass pieces weighing approximately 10–20 mg were placed in a Pt crucible and heated/cooled in the DSC. The same heating rate (20 K/min) was used for all the samples, but the cooling rates varied from 2 to 50 K/min to include the theoretical values of q_{cr} previously calculated by Cabral et al. [1]. The samples were then reheated to 50 °C above the liquidus temperatures and kept there for 5 min to ensure that the material had melted completely before each cooling run.

We performed several experiments for each glass and found different values for K_H and q_{cr}, which were taken as a measure of the method's experimental errors. The same procedure was adopted for the other samples and $\ln(q_{cr})$ vs. K_H was plotted for all the glasses.

To evaluate the effect of the crucible's material on the crystallization temperatures during cooling, T_c^c, three monolithic samples of LS_2 with approximately the same mass were successively heated and cooled in graphite, alumina and platinum crucibles. In all these cases, they were initially heated in a DSC crucible up to 40 °C at 5 K/min, kept for 5 min at that temperature and heated at 20 K/min up to 1200 °C. They were then cooled at rates of 2, 5, 8, 10 and 20 K/min, using an inert atmosphere of high purity argon. This procedure was repeated several times for each cooling rate. Since all the experimental parameters, such as the samples' mass, atmosphere, gas flow and heating/cooling rates were constant, the crystallization temperatures obtained during cooling could be compared.

4. Results

The objective of this work was to verify a possible relationship between vitrification ability and stability of glass-forming systems.

Except for the NC_2S_3 glass, the cooling traces of all the glasses showed several crystallization peaks, a typical phenomenon of surface (heterogeneous) crystallization. Typical cooling curves are shown in Fig. 1. To test the reproducibility of the crystallization temperatures during cooling, T_c^c, we successively heated/cooled a monolithic glass sample of LS_2 using a platinum crucible. This procedure was repeated from three to five times for each cooling rate. The crystallization temperatures are presented in Table 1. For cooling rates of 10–20 °C/min, the crystallization temperatures T_c^c
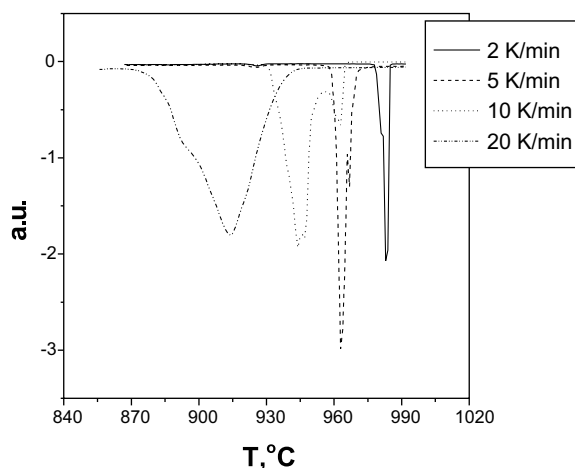

Fig. 1. DSC scans obtained for the LS_2 glass with different cooling rates, which are indicated on the right-hand side of the plot.

Table 1
Crystallization temperatures in repeated cooling experiments of the LS_2 glass cooled at different rates

Cooling rates (C/min)	T_c^c (°C)
2	983, 984, *979*, 988, 985, 989
5	967, *955*, 977, 970, 972, 981
8	970, 967, 976, 962, 962, *961*
10	963, 973, 959, 945, *912*
20	914, 905, 953, 920, *901*, 907

The minimum T_c^c obtained for each cooling rate is italicized.

varied by approximately 50–60 °C! For other cooling rates, variations of about 10–25 °C were observed. These substantial variations are clearly outside the range of instrumental error and demonstrate the sensitivity of heterogeneous crystallization to the presence of solid impurities (from the atmosphere), mechanical vibrations, etc. Upon cooling through the region of high growth rates ($T/T_m \sim 0.9$), any solid impurity or mechanical perturbation can induce fast crystallization of the melt. In addition, it is well known that platinum is an excellent catalyst for crystallization of LS_2, NC_2S_3 and probably of other glasses [5,9]. Since there is surface contact between the melts and the DSC crucibles, these provide a favorable pathway for heterogeneous surface crystallization, leading to irreproducible crystallization temperatures (shown in Table 1). Fortunately, however, this phenomenon does *not* occur upon heating; thus, the crystallization temperatures are perfectly reproducible. In heating experiments, the glassy samples are (mostly) homogeneously nucleated before they reach a region of substantial growth and then fully crystallize. In order to take heterogeneous crystallization on the cooling path into account, we propose *three modifications* for the CB method.

Using the same heating/cooling rates and different monolithic samples of each glass, we carried out at least three cooling experiments for each cooling rate. First, when more than one crystallization peak appeared on the cooling trace of a given DSC run, only the peak at the *highest temperature* (relating to the first phase to crystallize) was considered. We made this choice because, at lower temperatures, the sample already contained crystals. Second, considering all the tests with the same cooling rate, we took the *lowest* T_c^c peak (among the highest peak of each run) to favor internal (homogeneous) crystallization rather than heterogeneous crystallization. As an example, Fig. 2 shows some traces of a NC_2S_3 glass in which the crystallization temperatures varied significantly. Third, we calculated q_{cr} with the modified Eq. (3b). From the resulting crystallization temperatures for each cooling rate, plots of $\ln(q) \times 1/(\Delta T_c^c)^2$ were obtained for each glass. Using the respective melting temperatures, the critical cooling rates
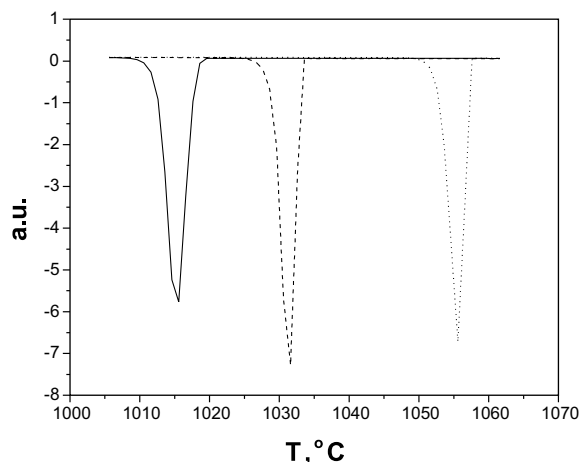
Fig. 2. Different DSC runs obtained during cooling of the same sample of NC_2S_3 glass at 15 K/min: (solid lines) first; (dashed line) second, and (dotted line) third run.
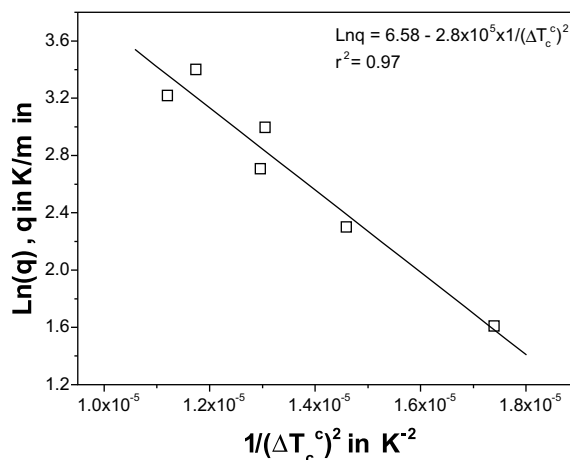

Fig. 3. $\ln q \times 1/(\Delta T_c^c)^2$ for the NC_2S_3 glass. The straight line equation and its r^2 are also shown.

Table 2
Intercepts, slopes, r^2 and the critical cooling rates obtained for each glass using Eqs. (3a) and (3b), respectively

System	A (K/min)	$B(K^2)$	r^2	q_{cr} (K/s), Eq. (3a)	q_{cr}^*, (K/s) Eq. (3b)
LS_2	3.2	9188.6	0.94	0.4 ± 0.1	0.4 ± 0.1
44NS	3.6	15724.4	0.97	0.6 ± 0.1	0.6 ± 0.1
LS_2-OH	4.3	19547.9	0.80	1.2 ± 0.3	1.2 ± 0.3
N_2CS_3	5.3	30077.6	0.92	3.3 ± 1	3.3 ± 1
NC_2S_3	6.6	287228.9	0.97	12 ± 2	11 ± 2
BS_2	7.1	320785.8	0.95	20 ± 3	18 ± 3
$Ba_2TiSi_2O_8$	8.2	398142.5	0.60	60 ± 39	53 ± 35

estimated by Eqs. (3a) and (3b) are presented in Table 2. As an example, Fig. 3 displays the data obtained in one experiment with NC_2S_3. According to the equation obtained from that figure and Eq. (3b): $q_{cr} \sim 11$ K/s.

5. Discussion

5.1. Critical cooling rates

The q_{cr} of Table 2 obtained from the two methods, Eqs. (3a) and (3b), are very close and are qualitatively consistent with our experimental observations in melting and cooling these seven glasses in the laboratory. Additionally, they indicate the same trend of GFA. In other words, LS_2 is

the easiest glass to make while the $Ba_2TiSi_2O_8$ melt must be powerfully pressed to avoid crystallization during cooling.

The present CB results for q_{cr} are about one order of magnitude greater than those previously calculated by the nose method [1]. However, it is known that the nose method overestimates q_{cr}. One could argue that these high q_{cr} differences result from the fact that the cooling rates used in this work are of the same order of magnitude of q_{cr}, in contrast with Colmenero and Barandiarán's [3] suggestion (the cooling rates employed must be at least two orders of magnitude lower than q_{cr}).

We should emphasize, however, that the cooling rates used by Wichard and Day [4] and Huang et al. [5] to measure q_{cr} with the CB technique varied between 50 and 400 °C/s, and 2 and 12 °C/s,

respectively. These values are of the same order of magnitude as the critical cooling rates obtained. Moreover, in the case of the $40Li_2O$–$60SiO_2$ glass, whose q_{cr} was measured both directly and by the CB method, the agreement between the CB and experimental value of q_{cr} was excellent. Therefore, Colmenero and Barandiarán's suggestion is apparently not required to ensure the accuracy of q_{cr} estimates.

In our opinion, the fact that the critical cooling rates calculated by the nose method are *lower* than those estimated by the CB method is due to heterogeneous nucleation of the melts on the Pt crucible walls, as discussed below.

The K_H values obtained for each glass are reported in Table 3. The typical measurement errors were about 5–40%. Fig. 4 was plotted from the critical cooling rates evaluated through Eq. (3b), q_{cr}^*, and the K_H values obtained for each glass. This figure comprises a 2 o.m. range of q_{cr}, $0.5 < q_{cr} < 50$, and indicates that a relationship between q_{cr} and K_H exists: the higher the K_H the lower the q_{cr}.

These results are contradictory to those of Ref. [2]. On the other hand, in a forthcoming paper, Avramov et al. [10] theoretically tested possible relationships between measures of glass stability and a criterion for glass-forming ability by computing non-isothermal crystallization kinetics for typical values of the main quantities that control nucleation and growth in silicate glasses. These quantities were the melting entropy and two kinetic parameters that control the viscosity (B and T_o in the Vogel–Fulcher–Tamman equation). The results demonstrate that glass stability and glass-forming ability are related concepts, thus reinforcing the present findings.
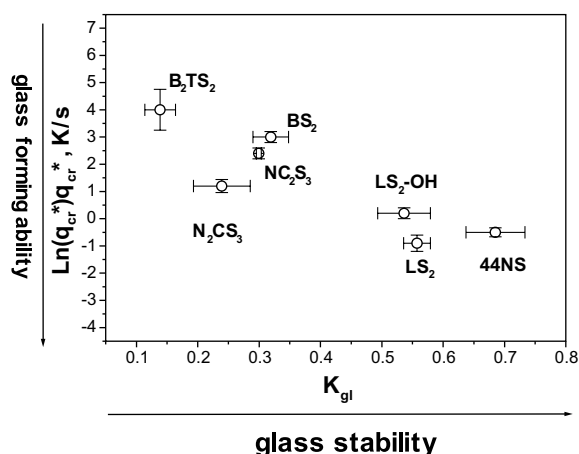

Fig. 4. $\ln(q_{cr}) \times K_H$ for the glasses studied. The error bars for q_{cr}^* refer to the standard deviation estimated from the best straight lines – $\ln(q)$ versus $1/\Delta T_c^2$ plots. The error bars for K_H correspond to the minimum and maximum values obtained for each glass.

5.2. Effect of the crucible material on q_{cr} and K_H

The crystallization temperatures obtained with the three types of crucibles were significantly different. As an example, the DSC traces obtained for the LS_2 glass cooled at 20 K/min are shown in Fig. 5. At all the cooling rates, the crystallization temperatures observed were lower for graphite than for alumina and platinum crucibles. This result can be explained by the fact that Pt and Al_2O_3 influence the crystallization temperatures of LS_2 (and probably of other systems), increasing and decreasing its q_{cr}, respectively. As a matter of fact, Pt is a powerful nucleating agent for LS_2, inducing heterogeneous nucleation at the crucible walls

Table 3
Onset temperatures from DSC curves recorded at 20 K/min and K_H parameter

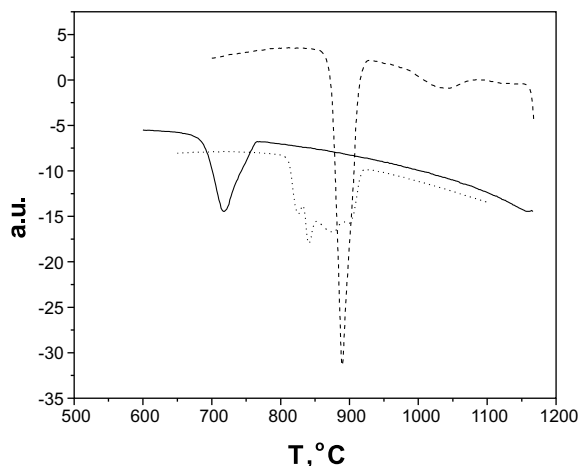| System	T_g (K)	T_c^h (K)	T_m (K)	K_H
44NS	694	903	1208	0.68 ± 0.05
LS_2	733	937	1303	0.56 ± 0.02
LS_2-OH	733	932	1303	0.54 ± 0.04
BS_2	975	1147	1686	0.32 ± 0.05
NC_2S_3	854	1016	1557	0.30 ± 0.04
N_2CS_3	755	883	1418	0.24 ± 0.03
$Ba_2TiSi_2O_8$	980	1068	1703	0.14 ± 0.03

Fig. 5. DSC scans obtained for a LS_2 glass cooled at 20 K/min in different crucibles: (solid line) graphite, (dashed line) alumina, and (dotted line) Pt.

[5,9,11]. On the other hand, it is well known that alumina (which probably dissolves in the melt) increases the glass viscosity, thereby decreasing crystal nucleation and growth rates [12].

Furthermore, in certain cooling experiments, we detected different crystallization temperatures (several crystallization peaks) in repeated experiments. However, we observed only one crystallization peak in graphite crucibles. The differences among these results clearly indicate heterogeneous crystallization induced by Pt and Al_2O_3 when the molten samples were in contact with the crucible walls. This behavior was not observed with the graphite crucible because this material, whose wettability is almost non-existent, did not react with the LS_2 glass. Indeed, at the end of the experiments, the samples presented a spherical shape while, in the Pt and Al_2O_3 crucibles, the samples were distributed around the crucible walls, wetting them.

Despite the crucible effect, the overall results of this research indicate that the K_H parameter, which is easy to measure, can be used to compare the relative vitrification tendency of good glass-forming systems. However, we demonstrated that the relationship between K_H and q_{cr} is valid only for glasses that show copious *internal* nucleation (in addition to surface nucleation). Therefore, due to

the crucible effect and to the sensitivity of both GS and GFA to the nucleation mechanism, extreme care with the experimental procedures must be exercised when measuring these parameters. It is reasonable to assume that this technique can also be applied to reluctant glass formers, such as metallic and fluoride glasses. In this case, for instance, variations of K_H with the addition of certain compounds to the base glass could be used to optimize glass-forming compositions.

6. Conclusions

The experimental critical cooling rates obtained by the CB technique, modified in this work to favor internal nucleation, were consistent with experimental observations on the melting and quenching of seven glass-forming liquids.

The critical cooling rates obtained by the CB method from experiments in Pt crucibles were one order of magnitude greater than those predicted from theoretical calculations using TTT curves. This result is due to heterogeneous nucleation on the Pt crucible walls. Despite this drawback, the critical cooling rates consistently varied with glass composition indicating that the CB method can be used to estimate the relative vitrification tendency and to compare different materials.

An empirical correlation between the Hrubÿ parameter of glass stability and the glass-forming tendency was demonstrated, in line with theoretical expectations.

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