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Can glass stability parameters infer glass forming ability?

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Abstract

Glass-forming ability (GFA) is the easiness to vitrify a liquid on cooling, while *glass stability* (GS) is the glass resistance against devitrification on heating; but it is questionable if there is any direct relationship between these two parameters. Therefore, to test this possibility, we assess and compare GFA and several GS parameters through quantitative criteria. GFA and GS were calculated for six stoichiometric glass forming oxides that only present surface (heterogeneous) crystallization in laboratory time scales: GeO_2, $Na_2O\cdot 2SiO_2$, $PbO\cdot SiO_2$, $CaO\cdot Al_2O_3\cdot 2SiO_2$, $CaO\cdot MgO\cdot 2SiO_2$ and $2MgO\cdot 2Al_2O_3\cdot 5SiO_2$; plus $Li_2O\cdot 2SiO_2$ and $Li_2O\cdot 2B_2O_3$ that, in addition to surface nucleation, also present homogeneous (internal) crystallization. We gauge GFA by the critical cooling rate, q_{cr}, which was calculated from an estimated number of heterogeneous nucleation sites per unit surface, N_s, and from experimental crystal growth rates, $u(T)$, assuming a detectable surface crystallized fraction $X_c = 0.001$. We define GS parameters by fourteen different combinations of the following characteristic differential thermal analysis (DTA) or differential scanning calorimetry (DSC) temperatures: the glass transition temperature (T_g), the onset crystallization temperature on heating (T_x^h), the peak crystallization temperature on heating (T_c^h), and the melting point (T_m). To obtain the experimental GS parameters for each glass we carried out DSC runs using coarse and fine powders, and completed the necessary data with literature values for T_m. The results for fine and coarse particles were quite similar. Most of the GS parameters that consist of three characteristic DSC temperatures show excellent correlation with GFA, however, rather poor correlations were observed for parameters that use only two characteristic temperatures. We thus demonstrated that certain, but not all GS parameters can be used to infer GFA.

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1. Introduction

There is now consensus that any material can vitrify if cooled from the molten state to the glass transition temperature, T_g, at a rate fast enough to prevent crystallization. The slowest a material can be cooled down to T_g without crystallization the easiest it is vitrified, and this property is denominated *glass forming ability* (GFA). A maximum allowed fraction of crystals, X_c, usually taken between 0.1% and 0.0001%, is conventionally assumed to classify a material as glassy. One can thus define a *critical cooling rate*, q_{cr}, to avoid a crystalline fraction higher than X_c on cooling a liquid. Therefore, q_{cr} gauges GFA. However, it is quite difficult to accurately measure q_{cr} and the complexity increases for reluctant glass formers that require very high cooling rates. If one could devise indirect ways to estimate GFA would then avoid exhaustive laboratory investigations, and this is thus a key step for efficient development of new glasses and glass-ceramics.

On the other hand, once a glass is made, for instance by fast quenching a melt, its stability against crystallization can be easily investigated. The resistance of a given glass

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against crystallization upon reheating defines *glass stability* (GS). GS is typically derived from characteristic temperatures that are determined from simple non-isothermal analyses, such as DTA or DSC. It is thus desirable to know how one can estimate GFA from GS measurements. However, the definitions of GS are somewhat arbitrary, only seldom have been rigorously tested and, as we will summarize below, it is controversial if there is any straightforward relationship between GFA and GS.

In this work, we experimentally test the existence of possible correlations between precisely calculated critical cooling rates (GFA) and fourteen ways to characterize GS using DSC. We use eight stoichiometric glasses: GeO_2 (G), $Na_2O \cdot 2SiO_2$ (NS_2), $CaO \cdot MgO \cdot 2SiO_2$ (CMS_2), $PbO \cdot SiO_2$ (PS), $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$ ($M_2A_2S_5$) and $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (CAS_2), which only show heterogeneous (surface) nucleation; plus $Li_2O \cdot 2SiO_2$ (LS_2) and $Li_2O \cdot 2B_2O_3$ (LB_2) that also show homogeneous (internal) nucleation in addition to predominant surface nucleation. Therefore, the paper's objective is to systematically verify possible relationships between GFA and GS parameters for glasses that crystallize via the most common nucleation mechanism, i.e. surface (heterogeneous) nucleation.

1.1. Literature review

1.1.1. Glass forming ability

A variety of theories have been proposed to understand why some systems easily vitrify while others do not [1,2]. Ultimately, a high *glass forming ability* is associated with slow crystallization rates. Uhlmann [3] was one of the first to use the concept of crystallization kinetics controlling glass formation. His method refers to *TTT* (time–temperature–transformation) diagrams, which are temperature versus time graphs showing curves that correspond to specified fractions of transformed phase. A curve in a *TTT* diagram shows how one can set a thermal treatment to achieve a given fraction of transformed phase. To vitrify a liquid by cooling, the crystallized fraction of interest is normally the smallest detectable, usually assumed to be 10^{-2}–10^{-6}. A 'nose' arises in the *TTT* diagrams at a temperature T_n and time t_n where the rate of transformation is the fastest. According to the *nose method*, the critical cooling rate for glass formation, q_{cr}^{n}, is given by

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

However, critical cooling rates calculated by the *nose method* are typically one order of magnitude greater than experimentally determined values [4]. Thus, this method can only be used to *estimate* relative critical cooling rates and to compare the glass forming ability of different materials.

It is quite laborious to experimentally build *TTT* curves, and it is yet not possible to theoretically calculate such curves due to the lack of an accurate expression for the nucleation rates. It is also rather difficult to directly measure critical cooling rates. To circumvent this problem, Colmenero and Barandiarán [5] proposed an experimental method to easily estimate q_{cr} by determining the crystallization temperatures when a liquid is cooled in a DTA or DSC equipment at different rates, q. Their method is here denominated CB. These authors suggested that on cooling a liquid, q is related to ΔT_c^c by

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

where $\Delta T_c^c = T_m - T_c^c$, T_c^c is the crystallization peak temperature on cooling, and A and B are empirical constants obtained from a straight line in $(\ln q)$ versus $1/(\Delta T_c^c)^2$ plots. If ΔT_c^c is extrapolated to infinity (no crystallization), q_{cr} can be determined from the intercept, A, of the line with the $\ln q$ axis. The physical meaning of Eq. (2) can be realized if we rewrite it using the classical formula of Turnbull for the thermodynamic driving force: $\Delta G(T_c^c) = \Delta S_m \Delta T_c^c$. Eq. (2) then becomes $\ln q = \ln q_0 - \frac{B \Delta S_m^2}{\Delta G(T_c^c)^2}$, where q_0 is a constant. Therefore, compositions having low $\Delta G(T_c^c)$ and high melting entropy, ΔS_m, should present low critical cooling rates and are thus good glass formers.

Only a few researchers have tested the CB method. For instance, Wichard and Day [6] determined the critical cooling rates for five compositions of the Ga_2O_3–CaO system using the CB method and also an alternative technique. This second method is here denominated WD, and consists of repeatedly heating up a thin layer of glass around a Pt–10% Rh thermocouple bead, cooling it down at different rates and then recording eventual exothermic crystallization peak temperatures on cooling in a temperature versus time graph. The crystallization peak is absent when the cooling rate is faster than q_{cr}. The critical cooling rate is then obtained from a ΔT_c^c versus $\log q$ plot for ΔT_c^c tending to infinity. Wichard and Day melted each composition between 150 and 250°C above its respective *liquidus* and cooled them at least 30 times at various rates to record exothermic crystallization peaks. The q_{cr} determined by the CB method (using a Pt crucible) and the experimental values agreed.

The WD method was afterwards used to determine critical cooling rates for CaO–Ga_2O_3–SiO_2 [7] and BaO–TiO_2–SiO_2 [8] glasses confirming the expected tendency of increasing GFA with increasing silica content.

Huang et al. [4] compared the CB and WD methods by studying the nucleating power of Pt, Au, P_2O_5 and TiO_2 in a $40Li_2O \cdot 60SiO_2$ glass. They showed that q_{cr} increases with the amount of Pt and Au added, but the effect of Pt is stronger than that of Au; while TiO_2 practically does not change the q_{cr}, and P_2O_5 decreases it. As regards to the WD method, the sample that yielded a smooth cooling curve (without any exothermic crystallization peak detected by a thermocouple) was checked by optical microscopy and the respective cooling rate was used to estimate q_{cr} when no crystals were detected. If some crystals were observed, the sample was melted again and cooled at a