Letter to the Editor

A simple method to predict the nucleation mechanism in glass

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Why does crystal nucleation occur in some glasses via the energetically unfavorable homogeneous mechanism? This intriguing question is the focus of this work.

It was demonstrated [1] that a simple rule of thumb can be used to distinguish the nucleation mechanism in several stoichiometric glass-forming systems. For compositions with small values of reduced glass transition temperatures, $T_g/T_f < 0.6$, the temperatures of maximum nucleation rates, T_{max}, are higher than T_g. These systems show homogeneous (internal) nucleation in laboratory timescales. On the other hand, for the majority of glasses, the typical values of reduced T_g are high i.e., $T_g/T_f > 0.6$, the calculated (by CNT) values of T_{max} are significantly below T_g, and only heterogeneous nucleation is observed. In this context, T_g refers to values calculated from the viscosity curves ($\eta = 10^{12}$ Pa s).

It was shown [2,3] that failure to detect homogeneous nucleation in glasses, for which $T_{max} < T_g$, is due to one or more of the following causes: low nucleation or growth rates and long induction times for nucleation in the temperature ranges where the predicted steady-state homogeneous nucleation rates would be maximum. To calculate these kinetic properties, however, one has to make several assumptions and to use theories which are not fully satisfactory.

It was unambiguously demonstrated [4] that glasses that exhibit homogeneous nucleation have both cation and anion arrangements which are very similar to their corresponding crystal phases, while the glass and crystal structures of glasses that only nucleate heterogeneously are quite distinct.

The objective of this communication is to present a simple way to predict the nucleation mechanism in glassy systems based on the following argument: if the structures of both glass and crystal phases are similar for compositions that nucleate homogenously, then it can be assumed that their mass densities, ρ, must be similar. For the other family of systems, large differences between the densities of glass and crystal could be expected, although it is possible that different structural arrangements can lead to comparable densities.

The densities of both glass and crystalline phases are compared in table 1 for various stoichiometric compositions belonging to both families. Although the data are not always reliable and were determined by different authors using different techniques and specimens [5–8], the general validity of the main argument of this paper can be envisaged. For glasses that nucleate homogeneously, the average difference in mass density is 3.4% with a maximum value of 7.7% (for $Li_2O \cdot SiO_2$), while for the other family of glasses average difference in density is much larger, 13.4%, with a maximum value of 33.7% (for B_2O_3).

Table 1
Densities of glass and crystal phases (g/cm^3)

System	Glass	Crystal	$\dfrac{\Delta\rho}{\rho\text{ glass}}$, %
Homogeneous nucleation			
$BaO \cdot 2SiO_2$	3.72	3.77 (lT)/3.73 (hT)	1.3/0.3
$Na_2O \cdot 2CaO \cdot 3SiO_2$	2.75	2.80	1.8
$CaO \cdot Al_2O_3 \cdot 2SiO_2$	2.70	2.76	2.2
$Na_2O \cdot SiO_2$	2.56	2.62	2.3
$2Na_2O \cdot CaO \cdot 3SiO_2$	2.66	2.76	3.8
$Li_2O \cdot 2SiO_2$	2.35	2.45	4.3
$CaO \cdot SiO_2$	2.90	3.09	6.6
$Li_2O \cdot SiO_2$	2.34	2.52 (ort)	7.7
Heterogeneous nucleation			
$K_2O \cdot 2SiO_2$	2.47	2.46/2.53	−0.6/2.4
$Na_2O \cdot 2SiO_2$	2.49	2.39/2.56	−3.7/3.1
$PbO \cdot SiO_2$	5.98	6.49	8.5
As_2S_3	3.17	3.46	9.1
P_2O_5	2.37	2.72	14.8
$Na_2O \cdot Al_2O_3 \cdot 6SiO_2$	2.28	2.62	14.9
GeO_2	3.65	4.23 (hex)	15.9
$CaO \cdot MgO \cdot 2SiO_2$	2.70	3.20	18.5
B_2O_3	1.84	2.46 (α)	33.7

At first sight, there appear to be 'exceptions' to the general rule, such as $K_2O \cdot 2SiO_2$, $Na_2O \cdot 2SiO_2$ (table 1) and silica glass (table 2). In the latter, several crystal phases have crystallographic modifications with densities quite close to the glass and only surface nucleation has been reported to occur.

Table 2
Mass densities of SiO_2 polimorphs

	Structure	ρ (g/cm^3)	$\dfrac{\Delta\rho}{\rho\text{ glass}}$, %
Glass	amor	2.20	–
β-Quartz	tri	2.65	20.4
α-Quartz	hex	2.53	15.0
γ-Trid.	ort	2.26	2.7
β-Trid.	hex	–	–
α-Trid.	hex	2.22	0.9
β-Cryst.	hex	2.32	5.5
α-Cryst.	cub	2.20	0.0

For glasses which nucleate homogeneously the densities of both phases (glass and crystal) are similar, and there are no 'exceptions' in table 1. Exceptions are only observed for systems that nucleate heterogeneously and can be explained in the following way: for these systems the densities of both phases tend to be quite different; however, they could be comparable (exceptions) for a few compositions since similar densities do not imply similar structures for glass and crystal. The opposite is true, i.e., different densities denote distinct structures.

Therefore, if the density difference between a given glass and its crystalline phase is large, say > 10%, it will most likely only nucleate heterogeneously. If the densities are comparable, nucleation could be homogeneous, although this condition alone is not sufficient to assure this type of nucleation. Thus, similar densities for glass and crystal is a *necessary* but *not sufficient* condition for structural similarity and inferentially for homogeneous nucleation.

References

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