

MOLECULAR STRUCTURE AND NUCLEATION IN GLASS

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ABSTRACT

The molecular structures of two metasilicate glasses which nucleate homogeneously (CaO.SiO_2 and $\text{Na}_2\text{O.SiO}_2$) as well as those of two glasses which only nucleate heterogeneously (PbO.SiO_2 and CaO.MgO.2SiO_2) were critically analyzed and compared with the structures of their equilibrium crystalline phases. It is shown that for the first class of glasses both cationic and anionic arrangements of glass and crystal are very similar. Moreover, the mass densities of both crystal and glass phases are comparable for such systems. The structural resemblance explain why these glasses readily nucleate homogeneously. For the second family of glasses, the structures and densities of glass and crystal are quite different and only heterogeneous nucleation is observed.

INTRODUCTION

Crystallization is a key issue to understanding glass formation. It also plays a fundamental role in the development of advanced glass-ceramics for biotechnology, electrooptics and other novel applications. In the absence of catalyzing agents, most supercooled liquids crystallize heterogeneously from the external surfaces when heated, however a few systems crystallize homogeneously in the bulk. Thus an intriguing question arises: Why does crystal nucleation occur in some glasses via the thermodynamically unfavorable homogeneous mechanism? This problem has been focused by the authors recently.

In a first study (ZANOTTO, 1987) it was demonstrated 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 time scales. 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 at the external surfaces or induced by catalyzing agents. In this context, T_g refers to values calculated from the viscosity curves ($\eta = 10^{12}$ Pa.s).

In a second work (ZANOTTO, WEINBERG & UHLMANN, 1989; ZANOTTO and WEINBERG, 1989) it was shown that the 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 mainly due to 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. Although the general trends described above are now firmly established, a crucial question, also raised by other authors (DICKINSON, 1989) remains: What is the relationship, if any, between the molecular structure of the supercooled liquid and its nucleation behaviour? In this paper we address this question by analyzing the structural details of several glass forming systems, belonging to both families mentioned above, as well as of their crystalline modifications, and correlate the nucleation mechanism with the anion and cation structures of glasses and crystals.

THE STRUCTURES OF GLASSES AND CRYSTALS

We shall restrict our considerations to glasses of simple stoichiometry whose crystal phases of identical composition are known. In order to compare the structures of glasses and crystals, we shall use structural data available in the literature, for the following metasilicates: $\text{Na}_2\text{O} \cdot \text{SiO}_2$, $\text{CaO} \cdot \text{SiO}_2$, $\text{PbO} \cdot \text{SiO}_2$ and $\text{MgO} \cdot \text{CaO} \cdot 2\text{SiO}_2$. The first two systems show homogeneous nucleation while the last two only nucleate heterogeneously (ZANOTTO, 1987; ZANOTTO, WEINBERG and UHLMANN 1989; ZANOTTO and WEINBERG, 1989). They all form chain silicates.

$\text{Na}_2\text{O} \cdot \text{SiO}_2$

In the case of the $\text{Na}_2\text{O} \cdot \text{SiO}_2$ system, X-ray diffraction (YASUI, HASEGAWA & IMAOKA, 1983), NMR studies (DUPREE, HOLLAND, McMILLAN & PETTIFAR, 1984; GRIMMER, MOGI, HOHNER, STADE, SAMOSON, WIEKER & LIPPMAA, 1984) and molecular dynamics simulations (INONE & YASUI, 1987) are available. All these papers confirm the similarity between the molecular structure of the glass and that of the crystalline metasilicate. They also confirm the existence of (SiO_4) chains, with alkali ions occupying certain sites between the chains. In particular, the bending angles between two adjacent tetrahedra within a chain agree very well ($\theta_g = 20^\circ$, $\theta_c = 21.2^\circ$). With regard to the coordination of the cations in the glass, a molecular dynamics simulation gives a sodium - oxygen distance of about 0.25 nm with a coordination number CN of about 7, whereas the structural model, satisfying the RDF, provides a more detailed picture of the sodium coordination. Four oxygen atoms have a distance between 0.236 and 0.244 nm but there are two further oxygen atoms participating partially in the sodium coordination with distances of 0.273 nm, and 0.332 nm, respectively.

The differences between the sodium coordination in the glass and in the $\text{Na}_4(\text{Si}_2\text{O}_6)$ crystal structure (GRUND & PIZY, 1952), a distorted trigonal bipyramidal coordination with distances between 0.227 and 0.245 nm, are not drastic and thus no obstruction should be expected for crystallization.

$\text{CaO} \cdot \text{SiO}_2$

The structure of $\text{CaO} \cdot \text{SiO}_2$ glasses was investigated by different methods: IR spectroscopy (BOBKOVA, 1979) X-ray diffraction and Raman spectroscopy (YIN, OKUNO, MORIKAWA, MARUMO & YAMANAKA, 1986) MASS NMR (KIRKPATRICK, DUNN, SCHRAMM, SMITH, OESTRIK & TURNER, 1986) and neutron diffraction (ECKERSLEY, GASKELL, BARNES & CHIEUX, 1988).

All papers emphasize the great similarity between the structures of glass and wollastonite. This means that the structure of the glass consists to a large extent of (SiO_4) tetrahedra chains, linked by calcium ions.

The coordination of Ca is very similar in both structures; the 0-17 NMR spectra are almost identical. The RDF, obtained by X-ray diffraction, indicates that Ca is surrounded by 6 oxygen atoms at an average distance of 0.234 nm and one further oxygen atom at 0.254 nm. Also the partial RDF of Ca, obtained by neutron diffraction for different Ca isotopes, confirms the similarity between the Ca coordination shell in glass and in wollastonite: the RDF provides a distance $r(\text{Ca-O}) = 0.237 \pm 0.012$ nm and $\text{CN} = 6.16 \pm 0.15$.

A majority of the coordination shells around Ca form octahedra of which only about one sixth are distorted, such that a seventh oxygen atom is within 0.250 and 0.285 nm from the calcium ion, causing a broad tail of the corresponding maximum in the RDF. Thus, the coordination number of Ca in the glass is probably slightly smaller than that in the crystal (HESSE, 1984). Here we refer to wollastonite 2 M, parawollastonite, where three different Ca sites exist: two of three sites possess a coordination shell with six oxygen atoms within the range of 0.224 to 0.254 nm, whereas the third Ca site has a seventh oxygen at a distance of 0.264 nm. Thus, an average coordination number of 6.33 results for the crystal structure.

Due to the higher charge of Ca in comparison with the alkali ions, a stronger influence of these cations is experienced by the intermediate range structure of the glass. Thus (ECKERSLEY, GASKELL, BARNES & CHIEUX 1988); Ca-Ca distance is very similar to that in the crystal, and the same edge-sharing arrangement of the octahedra around Ca takes place in the glass. Consequently, also in this case homogeneous nucleation is possible due to the excellent similarity between the structures of glass and crystal.

PbO.SiO₂

PbO.SiO₂ glasses were investigated by XPS (SMETS & LOMMEN, 1982), Si-29 NMR (LIPPMAA, SAMOSON, MOGI, TEEAAV, SCHRAML & GOTZ, 1982) and with XRD (IMAOKA, HASEGAWA & YASUI, 1982). Clear differences with respect to the structure of alamosite, Pb₁₂Si₁₂O₃₆, were detected in all studies. Although the glass structure is dominated by SiO₄ chains, the XPS study shows that the ratio between the number of non-bridging oxygens and the total number of oxygens is 0.40 in the glass. That is clearly higher than ratio 0.33 found in alamosite, which is typical for single chain silicates.

The Si-29 MAS NMR spectrum of the glass is also clearly distinct from the alamosite spectrum. In the crystal, three different signals are detected, corresponding to three clearly different distances between the central Si in the tetrahedra and the Pb ions in the complex folded silica chains. One signal is outside the usual range corresponding to Q² groups. The glass, on the other hand, shows only one signal in the range typical of single chain silicates. Therefore, by realizing more uniform distances to the silica tetrahedra, the glass structure allows a more regular coordination of Pb by oxygen than the alamosite or structure does. Thus, the formation of difficultly realizable "zwolfer" single chains, necessarily connected with crystallization, is hindered, and indeed, PbO.SiO₂ glasses only nucleate heterogeneously (ZANOTTO, 1987; ZANOTTO & WEINBERG, 1989).

CaO.MgO.2SiO₂

At least two investigations of the CaO.MgO.2SiO₂ (diopside) glass structure are known, by 0-17 MAS NMR (KIRKPATRICK, DUNN, SCHRAMM, SMITH, OESTRIK & TURNER, 1986) and by Raman spectroscopy (ETCHEPARE, 1972). Both papers describe well defined differences between the glass and diopside structures. The Raman bands corresponding to the silicate chain vibrations are comparable for glass and crystal. However, the vibrations of the cations are quite different. The NMR results also show that "wollastonite" like and "enstatite" like sites exist in the glass structure.

The silicate chains in wollastonite and enstatite are distinguished by their periodicities (enstatite P = 2, wollastonite P = 3). One can assume that the formation of chain segments of a definite warping is influenced by the cation size in such a way that the neighboring segment tends to have the same curvature preferentially. It means that the adjacent cation would be of the same kind, in contrast to the energetic long range compromise of the crystal, where an alternating occupation of the cation sites by Mg²⁺ and Ca²⁺ takes place, (although, surely, also other situations are imaginable where just an alternation of cation sites may be energetically

advantageous at molecular level). However in the case of diopside glass, the possible existence of precursors of a conceivable phase separation on a molecular level (actually in this case phase separation does not occur) seems to be responsible for the avoidance of homogeneous nucleation.

Other seven glass forming systems were analysed and the overall picture is confirmed; systems having similar structures for glass and crystal nucleate homogeneously and vice-versa. A full report of these findings will be published elsewhere (MULLER, HEIDE & ZANOTTO, 1991).

RELATIONSHIP BETWEEN STRUCTURE AND DENSITY

If the structures of both glass and crystal phases are similar for compositions which nucleate homogeneously, 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 crystal phases are compared in Table I 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 (CRC 1974; MAZURIN 1983; BANSAL & DOREMUS, 1986; FELTZ, 1983) the general validity of the main argument of this paper can be envisaged. For glasses which nucleate homogeneously, the average difference in mass density is only 3.4% with a maximum value of 7.7% (for $\text{Li}_2\text{O} \cdot \text{SiO}_2$) while for the other family of glasses the average difference in density is much larger, 13.4%, with a maximum value of 33.7% (for B_2O_3).

At first sight, there appears to be "exceptions" to the general rule, for glasses which nucleate heterogeneously, such as $\text{K}_2\text{O} \cdot 2\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$. For glasses which nucleate homogeneously the densities of both phases (glass and crystal) are similar, and there are no "exceptions" in Table I. Exceptions are only observed for systems which 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 factual i.e. different densities denote distinct structures.

CONCLUSIONS

The relationship between the nucleation behaviour and the anion and cation arrangements in the glass and crystal structures of several types of silicates has been clarified. As expected, the more similar these structures the higher the homogeneous nucleation tendency.

A simple way to predict the nucleation mechanism is provided by density measurements: If the density difference between a given glass and its crystal 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.

Table I. Densities of glass and crystal phases (g/cm³)

System	Homogeneous Nucleation		$\frac{\Delta \rho}{\rho \text{ glass}}$ %
	Glass	Crystal	
BaO.2SiO ₂	3.72	3.77(HT)/3.73 (hT)	1.3/0.3
Na ₂ O.2CaO.3SiO ₂	2.75	2.80	1.8
CaO.Al ₂ O ₃ .2SiO ₂	2.70	2.76	2.2
Na ₂ O.SiO ₂	2.56	2.62	2.3
2Na ₂ O.CaO.3SiO ₂	2.66	2.76	3.8
Li ₂ O.2SiO ₂	2.35	2.45	4.3
CaO.SiO ₂	2.90	3.09	6.6
Li ₂ O.SiO ₂	2.34	2.52 (ort)	7.7
	Heterogeneous Nucleation		
K ₂ O.2SiO ₂	2.47	2.46/2.53	-0.6/2.4
Na ₂ O.2SiO ₂	2.49	2.38/2.56	-3.7/3.1
PbO.SiO ₂	5.98	6.49	8.5
As ₂ S ₃	3.17	3.46	9.1
P ₂ O ₅	2.37	2.72	14.8
Na ₂ O.Al ₂ O ₃ .6SiO ₂	2.28	2.62	14.9
GeO ₂	3.65	4.23 (hex)	15.9
CaO.MgO.2SiO ₂	2.70	3.20	18.5
E ₂ O ₃	1.84	2.46 (α)	33.7

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