

## Molecular structure and nucleation in silicate glasses

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The molecular structures of several silicate glasses which nucleate homogeneously ( $\text{CaO}\cdot\text{SiO}_2$ ,  $\text{Na}_2\text{O}\cdot\text{SiO}_2$ ,  $\text{Li}_2\text{O}\cdot\text{SiO}_2$ ,  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ ,  $\text{BaO}\cdot 2\text{SiO}_2$  and  $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ ) as well as those of glasses which only nucleate heterogeneously ( $\text{PbO}\cdot\text{SiO}_2$ ,  $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ ,  $\text{CaO}\cdot\text{MgO}\cdot 2\text{SiO}_2$ ,  $\text{K}_2\text{O}\cdot\text{TiO}_2\cdot 3\text{SiO}_2$  and  $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ ) are critically analyzed and compared with the structures of their equilibrium crystalline phases. It is shown that, for the first class of glasses (displaying homogeneous nucleation), both cationic and anionic arrangements in glass and crystal are similar. In some cases, cation coordination requirements lead to the formation of chain segments of high mobility which favor homogeneous nucleation. For the second family of glasses, the structures of glass and crystal differ and only heterogeneous nucleation is observed.

### 1. Introduction

Crystallization is a key issue in understanding glass formation. It also plays a fundamental role in the development of advanced glass-ceramics for biotechnology, electro-optics and other novel applications. In the absence of catalyzing agents, most supercooled liquids crystallize heterogeneously from the external surfaces when heated, and only a few systems crystallize homogeneously in the bulk.

One of us [1] previously demonstrated that there are two classes of stoichiometric glass-forming systems. The first systems are able to nucleate homogeneously and the temperatures of maximum nucleation rate,  $T_{\text{max}}$ , are at or above the glass transition temperatures,  $T_g$ :  $T_{\text{max}} \geq T_g$ . These glasses have short induction times,  $\tau$ . The opposite behavior is observed for the other type of glasses, which only crystallize heterogeneously;

the theoretical temperatures of maximum homogeneous nucleation rates are below  $T_g$ , i.e.,  $T_{\text{max}} < T_g$ ,  $\tau$  is very long, and the homogeneous nucleation rates are probably low. This last point, however, cannot be proved yet due to the insufficient predictive power of the existing theories [1–3].

Although the general trends described above are now firmly established, a crucial question, also raised by other authors [4], remains: what is the relationship, if any, between the molecular structure of the supercooled liquid and its nucleation behavior? In this paper, we address this question by analyzing the structural details of several glass-forming systems. We look at both families mentioned above, including their crystalline modifications, and correlate these structures with nucleation behavior (homogeneous vs. heterogeneous).

The understanding of the nucleation process suggests the existence of a relationship between the molecular structure of the supercooled liquid and its nucleation behavior, if one considers the expression for the steady state nucleation rate,  $I$ , derived by Turnbull and Fisher [5]:

$$I = ZN^*D^*, \quad (1)$$

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where the Zeldovich factor,  $Z$ , is given by

$$Z = \left( \frac{W^* N_A}{3\pi RT} \right)^{1/2} \frac{1}{n^*};$$

$N_A$  is Avogadro's number,  $R$  is the gas constant,  $n^*$  is the number of atoms in a nucleus of critical size, and the number of critical nuclei  $N^*$  is given by  $N^* = N_0 \exp(-W^*/RT)$ , where  $N_0$  is the total number of molecules per unit volume. The rate of molecular rearrangement,  $D^*$ , is given by

$$D^* = \frac{kT}{h} O^* \exp(-\Delta G_D/RT), \quad (2)$$

where  $O^*$  is the number of molecules on the surface of the nucleus,  $k$  is Boltzmann's constant, and  $h$  is Planck's constant. This theory contains two energy parameters,  $W^*$  and  $\Delta G_D$ , dominating the temperature dependence of  $I$ . Both quantities depend upon structural parameters. The activation energy for molecular rearrangement,  $\Delta G_D$ , is determined by the size and shape of the structural units in the supercooled liquid, and, therefore, one has to discuss under what conditions these units are most favorable for nucleation.

The thermodynamic barrier to form a mole of critical nuclei,  $W^*$ , is determined by the differences between the structure of glass and crystal.  $W^*$  can be evaluated by considering the special case of isotropic, spherical nuclei:

$$W^* = \frac{16\pi\sigma^3}{3\Delta G_v^2}, \quad (3)$$

where  $\sigma$  is the interfacial free energy and  $\Delta G_v$  is the difference in the Gibbs free energy per unit volume between glass and crystal. Obviously, the more similar the structure of glass is to that of the crystal, the smaller will be  $W^*$ .

Thus, a structural similarity between glass and crystal should favour nucleation. It is important, therefore, to prove whether such similarity is in fact greater for glasses with homogeneous nucleation than for glasses with heterogeneous nucleation.

## 2. The molecular structure of some silicates

### 2.1. General remarks

The usual distinction between the structures of a glass and its corresponding crystal is the long range order of the crystal structure. However, a refined distinction is available from the inspection of local molecular structure. For instance, irregularities in the oxygen coordination polyhedra for cations such as  $\text{Li}^+$ ,  $\text{Na}^+$  or  $\text{Ca}^{++}$  arise from an energetic competition between local and overall ordering in silicate crystals. Such irregularities are indeed observed, although we know that, in the case of pure alkali and alkaline earth oxide crystals, the cations possess coordination shells of high regularity. Usually, the alkali oxides,  $\text{M}_2\text{O}$ , have an anti-fluorite structure and thus are formed by regular tetrahedra of oxygens around the alkali ions, whereas the alkaline earth oxides,  $\text{MO}$ , have a rock salt structure with regular octahedra.

In this paper, we will use the coordination polyhedra of the pure oxides, as a standard for the most regular coordination of the cations by the oxygen atoms. As demonstrated by Liebau [6(a)], these cations also prefer to form regular coordination shells in the crystalline silicates. Frequently, this tendency leads to strains and symmetry degradation of the  $[\text{SiO}_4]$  tetrahedra. In this connection, the results of the  $^{29}\text{Si}$  NMR investigations of Schneider et al. [7] are very interesting. They demonstrated that the symmetry of the  $(\text{SiO}_4)$  groups in a glass may be higher than in a crystal. For instance, they analyzed the case of  $\text{Q}^3$  sites (the superscript refers to the number of bridging oxygens per  $[\text{SiO}_4]$  tetrahedron) in tetrasilicates of Na and K, and found that such groups possess the ideal  $\text{C}^3$  symmetry only in the glass, because the lack of constraints in the liquid allow the local structure to relax to a higher symmetry.

Therefore, on a *molecular scale*, the silicate anions may, in some cases, have a higher symmetry in a glass than in the corresponding crystal! The same conclusion seems to be valid for the coordination shells of the modifying cations, if one considers recent EXAFS results by Greaves

et al. [8] and Calas et al. [9], or neutron diffraction results by Eckersley et al. [10(a), 10(b)]. These are discussed below in detail.

Initially, we can test the hypothesis that nucleation is favored by regularity at the molecular scale being substantially preserved during crystallization.

Certainly, such considerations are not absolutely new, although the previous focus of scientific interest has been biased to the anion structure, characterized by  $Q^n$  units (De Jong et al. [11], Schramm et al. [12]). For instance, Schramm et al. [12] claim that at least 60% of  $Q^n$  units must be preserved for crystallization to occur. We want to show that, in general, such a condition is not sufficient and that the *cations* also play an important role. In addition, we concentrate our attention on the *nucleation* process rather than on overall crystallization which also involves crystal growth.

In this paper, nucleation behavior is correlated with both the anion and cation structures of glasses and crystals. In fact, we concentrate on the cations, since they dominate the content of different  $Q^n$  units within the glass [13]. Liebau [6(b)] gives important chemical arguments (regarding electronegativity, valence and cation radius) for the influence of modifying cations on the conformation of silicate anions.

It should be emphasized that the majority of data analyzed throughout this paper refer to ambient temperature. Therefore, it is implicitly assumed that the high temperature structures (at  $T > T_g$ ) are not significantly changed when the crystals and glasses are quenched to ambient temperature. We shall restrict our considerations to glasses of simple stoichiometry whose crystal phases of identical composition are known and which are free of amorphous phase separation.

## 2.2. Silicate Systems with $Si:O = 1:3$ ('Metasilicates')

Let us consider metasilicate glasses. In this case the dominating anionic structural units are  $Q^2$  groups. Thus, we may expect to find parts of chains or rings in the glass. As demonstrated by Liebau [6(a)] these units possess good adaptability for different cation sizes by forming chains of

different periodicity in the crystalline state. In all cases, the flexibility of such chains will be better than that of two-dimensional layers or parts of three-dimensional networks.

In order to compare the structures of glasses and crystals, we shall use structural data available in the literature for the following metasilicates:  $Li_2O \cdot SiO_2$ ,  $Na_2O \cdot SiO_2$ ,  $CaO \cdot SiO_2$ ,  $PbO \cdot SiO_2$ ,  $MgO \cdot CaO \cdot 2SiO_2$  and  $K_2O \cdot TiO_2 \cdot 3SiO_2$ . The first three systems show homogeneous nucleation while the last three only nucleate heterogeneously [1,2,4].

With the exception of  $K_2Ti(Si_3O_9)$  with three-membered rings, the systems form chain silicates.  $Li_4(Si_2O_6)$ ,  $Na_4(Si_2O_6)$  and  $CaMg(Si_2O_6)$  (diopside) form single chains of periodicity  $P = 2$  ('zweier' single chains in the nomenclature of Liebau [6(a)]),  $Ca_3(Si_3O_9)$  (wollastonite) forms 'dreier' single chains ( $P = 3$ ), and  $Pb_{12}(Si_{12}O_{36})$  (alamosite) forms 'zwolfer' single chains. (In the case of  $CaO \cdot SiO_2$ , only the low-temperature modification of wollastonite contains single chains, whereas for silica-rich compositions, with higher values of  $T_g$ , the crystallization of pseudowollastonite, containing 'dreier' single rings, is also possible [14].)

### 2.2.1. $Na_2O \cdot SiO_2$

In the case of the  $Na_2O \cdot SiO_2$  system, X-ray diffraction [15], NMR spectra [16,17], and molecular dynamics simulations [18] are available. These papers confirm the similarity between the molecular structure of the glass and that of the crystalline metasilicate. They also confirm the existence of chains of  $(SiO_4)$  tetrahedra with alkali ions occupying certain sites between the chains. In particular, the bending angles between two adjacent tetrahedra within a chain agree very well ( $\theta_{gl} = 20^\circ$ ,  $\theta_{cr} = 21.2^\circ$ ).

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 radial distribution function (RDF), provides a more detailed picture of the sodium coordination. Four oxygen atoms have a distance between 0.236 and 0.244 nm (which compares very well with CN = 4

and  $r(\text{Na}-\text{O}) = 0.2403$  nm in crystalline  $\text{Na}_2\text{O}$ . There are, however, two further oxygen atoms participating partially in the sodium coordination with distances of 0.273 nm and 0.332 nm. Grund and Pizy [9] found a distorted trigonal bipyramidal coordination with distances between 0.227 and 0.245 nm.

The differences between the sodium coordination in the glass and in the  $\text{Na}_4(\text{Si}_2\text{O}_6)$  crystal structure are small and homogeneous nucleation is indeed observed [1,2].

### 2.2.2. $\text{Li}_2\text{O} \cdot \text{SiO}_2$

Information about the structure of  $\text{Li}_2\text{O} \cdot \text{SiO}_2$  glass is available from Yasui et al. [15]. Essentially the same similarity between the structures of glass and crystal is found as in the case of  $\text{Na}_2\text{O} \cdot \text{SiO}_2$ . There is a difference only in respect to the bending angles between the chain-building tetrahedra ( $0^\circ < \theta_{\text{gl}} < 8^\circ$ ,  $\theta_{\text{cr}} = 24.8^\circ$ ). However, in this connection, it is very interesting that a metastable structure of  $\text{Li}_4(\text{Si}_2\text{O}_6)$  was found by Barker et al. [20], which appears during the formation of the  $\text{Li}_4(\text{Si}_2\text{O}_6)$  crystal from the glass.

The observed change in the lattice constant,  $c_0$ , of the metastable phase with increasing temperature indicates a shrinkage of the chains, which leads to an increase of bending angle to  $16.5^\circ$ . Obviously, homogeneous nucleation is facilitated in this way, although the structures of the anionic units in the glass and in the crystal phase are still not absolutely identical.

With regard to the Li coordination in the glass, the modelling of the experimental RDF indicates four neighboring oxygen atoms within the range 0.205–0.222 nm and a fifth oxygen atom at 0.293 nm, in good agreement with the structure of  $\text{Li}_4(\text{Si}_2\text{O}_6)$  crystal ([21]: four oxygen atoms within the interval from 0.202 to 0.214 nm and a fifth oxygen atom at 0.258 nm).

Therefore, the modifier cation environments are similar in the glass and crystal phases and homogeneous nucleation is observed [1,2].

### 2.2.3. $\text{CaO} \cdot \text{SiO}_2$

The structure of  $\text{CaO} \cdot \text{SiO}_2$  glasses has been investigated by different methods: IR spectroscopy [14], X-ray diffraction and Raman spec-

troscopy [22], MAS-NMR [23], and neutron diffraction [10(a),10(b)]. All papers emphasize the great similarity between the structures of glass and the wollastonite crystal. This means that the structure of the glass consists to a large extent of  $(\text{SiO}_4)$  tetrahedra chains linked by calcium ions.

The coordination of Ca is very similar in both structures; the  $^{17}\text{O}$  NMR spectra are almost identical. (The same is true for Mg in the case of the  $\text{MgO} \cdot \text{SiO}_2$  glass in comparison with  $\text{Mg}_2(\text{Si}_2\text{O}_6)$  (enstatite). This point will be important in the discussion of the structure of  $\text{CaMg}(\text{Si}_2\text{O}_6)$  in the following section.)

The RDF, obtained by X-ray diffraction, indicates that Ca is surrounded by six 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  $r(\text{Ca}-\text{O}) = 0.237 \pm 0.012$  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 0.250–0.285 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 [24]. We refer here to wollastonite 2M, or parawollastonite, where three different Ca sites exist: two of three sites possess a coordination shell with six oxygen atoms within the range of 0.224–0.254 nm, whereas the third Ca site has a seventh oxygen at a distance of 0.264 nm. Thus, the crystal structure has an average coordination number of 6.33. In this case, the regular cation coordination in crystalline CaO ( $\text{CN} = 6$ ,  $r(\text{Ca}-\text{O}) = 0.24$  nm) resembles more the cation coordination in the silicate glass than in the crystalline silicate.

Due to the higher charge of  $\text{Ca}^{2+}$  in comparison with the alkali ions, a stronger influence of these cations is experienced by the intermediate range structure of the glass. Thus, Eckersley et al. [10(a),10(b)] found a Ca–Ca distance very similar to that in the crystal and the same edge-sharing arrangement of the octahedra.

Consequently, homogeneous nucleation is observed [1,2], consistent with the close similarity between the structures of glass and crystal.

#### 2.2.4. $PbO \cdot SiO_2$

$PbO \cdot SiO_2$  glasses were investigated by X-ray photoelectron spectroscopy (XPS) by Smets and Lommen [25], by  $^{29}Si$  nuclear magnetic resonance (NMR) by Lippmaa et al. [26], and by X-ray diffraction (XRD) by Imaoka et al. [27]. Clear differences with respect to the structure of alamosite,  $Pb_{12}Si_{12}O_{36}$ , were detected in all studies. Although the glass structure is dominated by  $SiO_4$  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 the ratio of 0.33 found in alamosite, which is typical for single chain silicates.

The  $^{29}Si$  MAS-NMR spectrum of the glass also differs from the alamosite spectrum. In the crystal, three different signals are detected, corresponding to three 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  $Q^2$  groups. The glass, on the other hand, shows only one slightly broadened signal in the range typical of single chain silicates. Therefore, by having more uniform coordination distances near the silica tetrahedra, the glass structure allows a more regular coordination of Pb by oxygen than does the alamosite structure. Thus, the difficult formation of 'zwolfer' single chains, necessary for crystallization, is hindered and, indeed,  $PbO \cdot SiO_2$  glasses only nucleate heterogeneously [1,2].

#### 2.2.5. $CaO \cdot MgO \cdot 2SiO_2$

At least two investigations of the  $CaO \cdot MgO \cdot 2SiO_2$  (diopside) glass structure are known, by  $^{17}O$  MAS-NMR by Kirkpatrick et al. [23] and by Raman spectroscopy by Etchepare [28]. Both papers describe well defined differences between the glass and the crystalline 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 preferentially have the same curvature. Thus the adjacent cation would be of the same type, by contrast with the long range energetics of the crystal, where an alternating occupation of the cation sites by  $Mg^{+2}$  and  $Ca^{+2}$  takes place. In the case of diopside glass, phase separation does not occur although the phenomenon of molecular level precursors to phase separation appears to be responsible for the avoidance of homogeneous nucleation.

#### 2.2.6. $K_2O \cdot TiO_2 \cdot 3SiO_2$

The structure of a  $K_2O \cdot TiO_2 \cdot 3SiO_2$  glass was studied by Raman and Ti K-edge X-ray absorption spectroscopy by Dickinson [4]. He concluded that there is a significant difference in the structure of crystalline and glassy phases. The structure of the crystalline specimen is typical of the short range order of  $Q^2$  groups and the intermediate range order of ring silicates. The glass instead contains higher polymeric species (1 NBO) as well as species with 2 non-bridging oxygens (NBOs). The coordination of Ti is between five and six in the glass and differs from the regular sixfold octahedron of the crystal. This glass only nucleates heterogeneously.

Summarizing the analyses of data available for the structure of glasses and crystals with  $Si:O = 1:3$ , we conclude that homogeneous crystallization occurs in the absence of drastic changes of either the cation or anion coordination.

### 2.3. Silicate systems with $Si:O = 2:5$ ('disilicates')

In the case of 'disilicate' glasses, information about both glass and crystal structures as well as on the crystallization behavior are available for  $Li_2O \cdot 2SiO_2$ ,  $Na_2O \cdot 2SiO_2$  and  $BaO \cdot 2SiO_2$ . The first and the latter glasses crystallize homoge-

neously, whereas  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  has a heterogeneous crystallization behavior [1–3].

The glass structures were investigated by several X-ray and neutron diffraction techniques ( $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  [29];  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  [8,30];  $\text{BaO} \cdot 2\text{SiO}_2$  [31]), by NMR [12,14,16,17,32] and by Raman spectroscopy [33]. Although the results are not completely consistent with each other, various structural concepts emerge.

### 2.3.1. $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$

For  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ , the majority of the results confirm a strong equivalence between the structures of glass and crystal. In the crystal structure [34], strongly folded layers consisting of six-membered rings, the so-called unbranched zweier single layers, are found. Parts of such layers are detected in the glass structure, too. The coordination number of  $\text{Li}^+$  ions between those layers is four in both cases. In the crystal, a relatively regular pyramidal  $\text{Li}^+$  coordination is found ( $r(\text{Li}-\text{O})$ : 0.185 nm; 0.188 nm; 0.199 nm; 0.204 nm). Recently, a metastable structure of lithium disilicate was found which presents an almost tetrahedral coordination of Li by oxygen [53]. This glass nucleates homogeneously [1,2].

### 2.3.2. $\text{BaO} \cdot 2\text{SiO}_2$

Strongly folded layers of six-membered rings are found in the structure of  $\text{BaO} \cdot 2\text{SiO}_2$  glass. In addition, the distance  $r(\text{Ba}-\text{O}) = 0.275$  nm is close to the Ba–O distance in sanbornite (IT- $\text{BaSi}_2\text{O}_5$ ) with an average value of 0.289 nm. In the very similar high temperature (hT) modification of  $\text{Ba}(\text{Si}_2\text{O}_5)$ , two different Ba sites exist with mean Ba–O distances of 0.283 and 0.291 nm [35]. The distances in the glass agree even better with the Ba–O distance in crystalline BaO (0.276 nm). However, the coordination number in the oxide is six while in  $\text{Ba}(\text{Si}_2\text{O}_5)$  it is eight and nine. The coordination number of Ba in the glass has not been determined explicitly.

The Ba–Ba distances are smaller in the glass than in the crystal structure of sanbornite, i.e., 0.42 versus 0.46 nm. Therefore the layer structures in the glass are more warped than in the crystal. That may imply that the coordination number of Ba is smaller in the glass, as suggested

by the distance  $r(\text{Ba}-\text{O})$ , which corresponds exactly to the sum of the ion radii of  $\text{O}^{2-}$  and  $\text{Ba}^{2+}$  for CN = 6. A similar interpretation is possible by comparing the Ba coordination in the glass with that of the crystalline (low temperature) IT and hT modifications. The smaller CN = 8 occurs only for one Ba site of the hT form (which is expected to be most similar to the glass structure) whereas in the IT form only CN = 9 occurs. On the other hand, Hesse and Liebau [35] emphasize that the tetrahedral layers of the hT form are less corrugated than in the IT form. Overall, the structures of glass and crystal are quite similar and homogeneous nucleation is observed [1,2].

### 2.3.3. $\text{NaO}_2 \cdot 2\text{SiO}_2$

In the  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  system, significant differences exist between the hT modification of  $\text{Na}_2(\text{Si}_2\text{O}_5)$  [36], and the IT phase [37], in regard to the magnitude of the layer warping as well as the directedness [6] of the non-bridging oxygen atoms. Also, the coordination of the sodium ions differs: in the hT  $\text{Na}_2(\text{Si}_2\text{O}_5)$  a distorted trigonal bipyramidal coordination occurs with four oxygen atoms within the range of 0.229–0.239 nm and a further oxygen at 0.260 nm. In the structure of IT  $\text{Na}_2(\text{Si}_2\text{O}_5)$  two different  $\text{Na}^+$  sites exist, the first being five-coordinated (0.231–0.259 nm) and the second being six-coordinated (0.238–0.257 nm).

For  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  glass, the RDF obtained by the X-ray diffraction studies of Imaoka et al. [30] confirms the existence of layer-like regions consisting of six-membered rings. The layer structure is somewhat similar to the structure of I- $\text{Na}_2(\text{Si}_2\text{O}_5)$ . In a model structure consistent with the experimental RDF of the glass, the sodium ions are coordinated by three non-bridging and one bridging oxygen atom, whereas the EXAFS results of Greaves et al. [8] yield a coordination number  $\text{CN} = 5.0 \pm 0.5$ , with a sharply defined distance  $r(\text{Na}-\text{O}) = (0.230 \pm 0.003)$  nm, implying again that the coordination of the cation is clearly more regular in the glass than in the crystal.

The  $^{29}\text{Si}$  and  $^{23}\text{Na}$  NMR spectra obtained by Dupree et al. [16] also reveal significant differences between the spectra of glass and crystal, by contrast with the corresponding ‘metasilicate’ systems where the  $^{29}\text{Si}$  spectra of glass and crystal

are similar. The interpretation of these authors directly addresses the aim of our paper: the glass structure may be considered more relaxed than that of crystal, i.e., the constraint of long range order in the crystal imposes some bond-angle strain and non-optimized coordinations which are absent in the glass. It is possible that the resistance to crystallization of some glasses arises from the necessity to locally increase free energies in the structure to produce the long-range order associated with the crystalline form of overall lower free energy.

On the other hand, the  $^{29}\text{Si}$  NMR results of Dupree et al. [16] and also that of Grimmer et al. [17] emphasize that both crystal and glass of  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  and  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  compositions contain only  $\text{Q}^3$  units. However, the more recent studies of Stebbins [13] and Schramm et al. [12] demonstrate, by the same method, that equilibria such as  $2\text{Q}^3 \rightleftharpoons \text{Q}^4 + \text{Q}^2$  take place, depending on the glass transition temperature and field strength of the cations. Such structural disproportionation reactions were also considered by De Jong et al. [11] based on their X-ray emission spectroscopy studies. It is important to point out that Stebbins [13] detected only a relatively small amount of  $\text{Q}^4$  groups (6.4% ( $T_g = 450^\circ\text{C}$ ), 7.9% ( $T_g = 530^\circ\text{C}$ )) in  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  in comparison with the value of 11.5% for  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ , while Schramm et al. [12] found 14.6%  $\text{Q}^4$  groups for  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ .

Therefore, neglecting the overall structural aspects and considering only the  $\text{Q}^n$  units, the structure of the  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  glass is more similar to its crystal structure (which contains only  $\text{Q}^3$  units) than that of the  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  system. In the case of strongly folded layers, such as those in the crystal structures of  $\text{Li}_2(\text{Si}_2\text{O}_5)$  and  $\text{Na}_2(\text{Si}_2\text{O}_5)$ , it is possible that the existence of  $\text{Q}^4$  groups in the glass favors crystalline layer formation because an occasional occurrence of  $\text{Q}^4$  groups, i.e., of joints between parts of two layers, may favor the needed warping of such layers.

#### 2.3.4. Comparison between $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ and $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$

Possibly the most important factor controlling crystallization behavior is the relationship be-

tween lithium ion size and its coordination. One can note that the lithium ion, due to its smaller cation radius and consequently its higher field strength, in comparison to sodium, may have a stronger tendency to form chain segments in order to achieve an optimum coordination. The formation of  $\text{Q}^4$  units is connected with the formation of  $\text{Q}^2$  units (see above) and the  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass contains more  $\text{Q}^2$  groups than  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  (Schramm et al. [12] found 21.9%  $\text{Q}^2$  groups in a  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass). In particular, the  $(\text{Si}_2\text{O}_5)$  layer structure enables only a pyramidal coordination, whereas the  $(\text{SiO}_3)$  chains render possible a tetrahedral coordination. This phenomenon may not be disadvantageous for crystallization (despite the differences in the  $\text{Q}^n$  groups between glass and crystal), because of the better mobility of structural units consisting of  $\text{Q}^2$  groups compared with  $\text{Q}^3$  groups. This type of structural disproportionation reaction might diminish  $\Delta G_D$ . This interpretation is quite speculative but will be reinforced by further arguments.

In any case, with the exception of the  $\text{Q}^n$  units, lithium disilicate possesses a close structural similarity (specially the network modifiers environment) between glass and crystal while the Na system bears considerable differences. The first nucleates homogeneously while the latter only nucleates heterogeneously [1,2].

#### 2.3.5. The role of network modifiers

We note the strong tendency to form chains in compositions which typically form  $\text{Q}^3$  units, e.g., the case of  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ . Systematic investigations of variations in  $\text{Li}_2\text{O}$  content, by Schramm et al. [12], show that, even within the wide composition range of 15–25 mol%  $\text{Li}_2\text{O}$ , a characteristic fraction of  $\text{Q}^2$  units exist (10–20%). Obviously, even in the case of small amounts of cations, the glass structure tends to optimize the coordination of the cations, in particular those of high field strength, by allowing local structures which differ from the main structure.

In this regard, Schramm et al. [12] assume the existence of attractive interactions between lithium ions in silicate glasses. Obviously, 'attractive interactions' between ions of the same charge are realizable only in an indirect manner, men-

tioned already in the discussion of the structure of the  $\text{MgO} \cdot \text{CaO} \cdot 2\text{SiO}_2$  glasses. Chain segments with relatively uniform bending angles between the tetrahedra, resulting from the influence of a certain cation, can cause the adjacent chain segment to tend to assume a comparable curvature, thereby favoring the coordination of the same cation specie in much the same way. Navrotsky et al. [54] give more detailed explanations based upon molecular orbital calculations, for the influence of cations on the silicate framework, confirming our general arguments.

By considering the consequences of the existence of different  $Q^n$  units in the comparison of  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  and  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ , glasses, one can clearly understand the *dominating influence of modifier cation* with respect to crystallization. Obviously, in these glasses, some cations are partially coordinated by  $(\text{SiO}_3)$  chains, in addition to the cations coordinated by  $Q^n$  units. Evidently, crystallization is promoted by the existence of the more mobile chain sections in the case of  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ . Thus one may conclude that the local gain in free energy by forming molecular chain units in the glass, which are inconsistent with the final crystal structure, is compensated by forming crystalline long range order. Consequently, no hindrance of crystallization is observed.

In the case of  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ , the local gain in free energy, caused by coordinating  $\text{Na}^+$  by chains of molecular dimensions, is lower than for  $\text{Li}^+$  (fewer units of high mobility) and can be compensated by crystallization. However it requires structural compromises in respect to the  $\text{Na}^+$  coordination, which reduces the crystallization tendency. For  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ , a higher gain of free energy occurs by forming 'molecular' chain units to coordinate  $\text{Li}^+$ . However, the formation of long range order would lead to strains on the silica layers and the free energy gain would no longer be compensated by crystallization. Hence, other forms of long range order are realized, preserving the 'molecular' chain structures and continuing the disproportionation of the  $Q^m$  groups. This ultimately may lead to crystallization of two phases.

Therefore, the coordination demands of the modifier cations play an important role in the

nucleation behavior of silicate glasses and can prevent the homogeneous crystallization of stoichiometric compounds, even when the differences between the  $Q^n$  groups are not drastic. In this respect, the influence of  $M^{2+}$  is stronger than that of  $M^+$ , and that of smaller cations is stronger than that of larger ones.

Thus, in addition to our considerations about the influence of the structure of glasses and crystals on the crystallization behavior of 'metasilicate' glasses, as discussed in the previous section, the results for disilicate glasses provide the following conclusions.

(i) The similarity (or difference) in the degree of  $Q^n$  units between melt and crystal is not sufficient to understand the differences in nucleation.

(ii) In addition, it is not enough to consider the attainability of a regular cation coordination in the crystal. It is also necessary to consider the differences in the disproportionation effects of the cations on the silica network of the glass which can (presumably) lead to structural units of higher mobility.

For brevity, we did not discuss the analogous mechanism of disproportionation in the case of chain silicates,  $2Q^2 \rightleftharpoons Q^1 + Q^3$ . However, we suppose that it does not play such an important role because the restrictions of a silica chain with respect to the possibilities to coordinate the cations are less than those of silicate layers. Therefore, the tendency for disproportionation will be smaller. In the following section, we consider structures which contain only  $Q^4$  units; in this case disproportionation is not possible.

#### 2.4. Feldspar systems

The structure of albite ( $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ) and anorthite ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) glasses were investigated by X-ray diffraction [38–41], EXAFS [42], Raman spectroscopy [43],  $^{27}\text{Al}$  NMR [44,23] and by  $^{29}\text{Si}$  NMR [45–47]. Although there are discrepancies among some of these studies, various aspects of the glass structure allow the differences in nucleation behavior (albite: heterogeneous; anorthite: homogeneous) to be discussed. From the RDF it is clear that these two glasses have different anionic (intermediate) range struc-

tures. In anorthite glass, four-membered rings are found, which are also present in the assemblage of the crystalline feldspar structure [6]. Albite glass, however, contains six-membered rings (like tridymite and nepheline) which are not compatible with its crystalline feldspar structure.

The investigations of Taylor and co-workers [38(a),38(b),39] show that the addition of  $\text{NaAlO}_2$  does not change the six-membered ring structure of the  $\text{SiO}_2$  liquid. With a decrease of the  $\text{Al}_2\text{O}_3$  content, however, McKeown et al. [42] found a transition to four-membered rings which appear in the structure of  $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$  [48].

A comparison of the cation coordination also yields arguments to illustrate the different nucleation mechanisms for anorthite and albite. In the case of albite glass, EXAFS results show a relatively uniform coordination of  $\text{Na}^+$  by about six oxygen atoms within a distance range from 0.256 to 0.262 nm. The extremely irregular coordination of  $\text{Na}^+$  in both modifications of crystalline albite, however, illustrate that the formation of long range order, joined with the transition from six-membered to four-membered rings of  $(\text{SiO}_4)$ , is achieved at the expense of the  $\text{Na}^+$  coordination. It would be interesting to know the nucleation behavior of glassy potassium feldspars (microcline, sanidine) and, particularly, of rubidium feldspar, where a more regular coordination of the alkali cations is possible within the crystalline feldspar structure. Additionally, Taylor and Brown [38(a)] established that six-membered rings exist in sanidine glass, which are incompatible with the structure of crystalline microcline and sanidine.

In the case of  $\text{Ca}^{2+}$  coordination, one finds an interesting situation in  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  glass. Taylor and Brown [38(a)] found Ca–O distances within the interval of 0.23–0.25 nm and a coordination number of about seven. There are three known crystalline modifications of this composition. Besides the stable 1T form of the triclinic anorthite, two metastable hT forms exist, a hexagonal [49] and a monoclinic double-layer form [50]. The cation coordination in these structures is clearly more regular than in the sodium feldspar.

In the hexagonal high temperature structure,

one finds a nearly undistorted coordination of  $\text{Ca}^{2+}$  by six O at  $0.239 \pm 0.002$  nm, forming a trigonal antiprism. In the monoclinic form, two statistically occupied Ca sites exist with coordination number of six, at a distance between 0.235 and 0.262 nm, and from 0.231 to 0.271 nm, respectively. The mean Ca–O distance in the 1T anorthite is 0.250 nm and, according to Kempster et al. [51], the cation site has a quite normal value of the temperature factor ( $1.0 \text{ \AA}$ ), indicating the strong influence of the alkaline-earth cations on structure formation. This promotes crystallization because an energetically favorable cation coordination is possible. The refinement of the anorthite structure [52] gives a more detailed, but similar picture.

With respect to the  $\text{Al}^{3+}$  coordination, all the techniques used confirm that only fourfold coordinated  $\text{Al}^{3+}$  occurs in the glass structures of anorthite and albite glass; however, Kirkpatrick et al. [23] have shown that the relatively broad  $^{27}\text{Al}$  NMR spectrum of the glass agrees well with the spectrum of crystalline anorthite (with eight different Al sites), demonstrating again a closer relationship between the glass and crystal structures of anorthite with respect to the  $\text{Al}^{3+}$  coordination.

The results of various  $^{29}\text{Si}$  NMR investigations differ with regard to the Al–Si distribution, describable by  $Q_m^n$  units [46], where, in the usual manner,  $n$  refers to the number of bridging oxygen atoms and  $m$  gives the number of the nearest aluminum atoms. Engelhardt et al. [46] found that the structure of anorthite glass is dominated by  $Q_4^4$  units as in the crystal. Studying the same system, De Jong et al. [45] describe a distribution of  $Q_m^4$  groups, i.e. mainly  $2 \leq m \leq 4$  (the authors used another nomenclature: their  $Q_i$  units correspond to the usual  $Q_{4-i}^4$  groups). These develop a distinct maximum at  $Q_4^4$  only after an intensive devitrification treatment. According to De Jong et al. [45], however, albite has 67%  $Q_1^4$  and 33%  $Q_2^4$  units in the crystal structure, and accommodate a broad distribution ( $0 \leq m \leq 3$ ) in the glass. These authors ascribe the differences in crystallization behavior between albite and anorthite alone to these differences in the  $Q_m^4$  distribution, assuming that these differences are reflected by

different growth rates (they did not discuss the nucleation behavior).

Obviously, these influences, caused by different  $\text{Al}^{3+}$  contents and, consequently, by different amounts of Al–O bonds, are important for crystallization. One should note that Al–O bonds are less difficult to break than Si–O bonds. We believe that the same considerations discussed at the end of the previous chapter are valid here also. The sole existence of chain units of high mobility is not sufficient to induce homogeneous nucleation if, concurrently, a sufficient energy gain is not realizable by attaining long range order. However, with regard to the coordination of the anions, a clear difference exists between albite and anorthite.

Thus, to understand the crystallization behavior, one has to take into consideration all these aspects, since there are no drastic differences between the  $\text{Al}^{3+}$  coordination in glass and crystal. Therefore, the different crystallization behavior of albite and anorthite also confirms our conclusions about the importance of a close similarity between the anionic and specially the cationic structure of the glass and the corresponding crystal for homogeneous nucleation. If, as in the case of albite, the energetic optimization on a molecular level leads to structural units quite different from those in the crystal, and if the need to reconstruct such units, in order to attain long range order, is accomplished by a clear deterioration of the cation coordination, the hindrance of homogeneous nucleation can be explained without taking into account the differences of Al content, although the latter also plays an important role.

### 3. 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 degree of similarity of these structures correlates with the tendency for the homogeneous nucleation.

The role of the *modifier cations* on nucleation

behavior has been emphasized. One simple reason for that influence is that the weaker bonds between these cations and the oxygen atoms (compared with those between silicon and oxygen) leads to a more ‘relaxed’ short range structure in the glass as ‘perceived’ by the cation environment as opposed to the strongly bounded and more rigid anion structures. The anion structures reveal their relaxation only at middle range distances, where the structural information, from RDF or other techniques, are less reliable. Other systems exist which display a similar behaviour to those shown here and will be discussed in a future paper.

An important implication of the present article may affect the Classical Nucleation Theory, which assumes a *step-by-step* atomic displacement for the birth of a critical nucleus. The structural similarity between glass and crystal for homogeneous nucleation allows one to speculate that a *cooperative rearrangement* of atoms might be involved in such a process. It remains to be proved whether it is possible to construct a theory based on this different mechanism.

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