

## **Influence of cation coordination on nucleation in silicate glasses\***

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*Dedicated to Prof. Dr. Friedrich Liebau on occasion of his 65th birthday*

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**Abstract.** By comparing the available structural parameters of silicate glasses and crystals of the same composition, the correlations between the nucleation behaviour of a glass and its short and middle range order, specially the coordination of the modifier cations, are discussed. There are glass systems which nucleate homogeneously ( $\text{Li}_2\text{O} \cdot \text{SiO}_2$ ,  $\text{Na}_2\text{O} \cdot \text{SiO}_2$ ,  $\text{CaO} \cdot \text{SiO}_2$ ,  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ ,  $\text{BaO} \cdot 2\text{SiO}_2$ ,  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) and systems which nucleate only heterogeneously ( $\text{PbO} \cdot \text{SiO}_2$ ,  $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ ,  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ ,  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ ).

It is demonstrated that changes in the cation coordination during the formation of the long range order play an important role for nucleation behaviour.

### **Introduction**

Liebau dedicated about one third of his excellent book (Liebau 1985) to the influence of the non-tetrahedral cations on the structure of the silicate

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anions in crystals, i.e. to the influence of those cations which are simply called “network modifiers” in the theory of glass structures (Vogel 1983). In the classical network model of silicate glasses those cations, first of all, have to compensate for excess negative charges, and are also responsible for the fission of oxygen bridges in the silica network, and thus play only a “destructive” role from the point of view of the network structure.

On the other hand, these cations also exercise a systematic influences on the structure of the crystalline “networks” mentioned above. Today further results of investigations on the environments of the modifier cations in glasses are available, which we will discuss later in detail and which illustrate that the consideration of the silicate anions of glasses alone is a very one-sided point of view.

The aim of our paper is in particular to show which role the coordination of the modifier cations plays in respect to the nucleation of silicate glasses. Because of the rather limited quantity of exact glass structure data available today our paper has only the character of a sketch.

It is well known that the nucleation of glasses is determined by different mechanisms. In the absence of catalysts, most glasses crystallize heterogeneously from the external surface, and only a few systems crystallize homogeneously in the bulk. To interpret these differences, hitherto first of all thermodynamic and kinetic parameters are considered (see e.g.: Zanotto and Weinberg 1989; Weinberg and Zanotto 1989).

But taking into consideration the expression for the steady state nucleation rate  $J$ , derived by Turnbull and Fisher (1949), one needs two energy parameters,  $W^*$  and  $\Delta G_D$ , the thermodynamic barrier to form critical nuclei and the activation energy for molecular rearrangement, respectively. Both parameters depend at a “molecular” level upon the glass structure as well as upon its relation to the crystal structure of the corresponding chemical composition, since  $\Delta G_D$  is determined by size and shape of the structural units in the supercooled liquid, and  $W^*$  decreases with a decreasing interfacial free energy between glass and crystal. The latter must become very small, if the short and middle range order of glass and crystal become very similar.

We will therefore try to understand the nucleation behaviour qualitatively by a comparison of the “molecular” structure of silicate glass with crystal.

## Results

In order to be able to compare the structures of glasses and crystals we have to restrict our considerations to glasses of simple stoichiometry. The following glass systems are included in the comparison of the structures:

– silicate glasses in which homogeneous nucleation is observed (Zanotto and Weinberg 1989):

$\text{Li}_2\text{O} \cdot \text{SiO}_2$ ;  $\text{Na}_2\text{O} \cdot \text{SiO}_2$ ;  $\text{CaO} \cdot \text{SiO}_2$ ;  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ ;  $\text{BaO} \cdot 2\text{SiO}_2$ ;  
 $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ .

– silicate glasses which nucleate only heterogeneously [or which do not nucleate in one uniform phase (\*)]:

$\text{PbO} \cdot \text{SiO}_2$ ;  $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ ;  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ ;  $\text{CaO} \cdot 2\text{SiO}_2$  (\*);  
 $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ .

In all these cases, structural parameters of glasses obtained by X-ray or neutron diffraction, EXAFS, NMR or molecular dynamic simulations are available in the literature and can be used to test, whether there are correlations between the nucleation behaviour on the one hand, and similarities in the structures of glass and crystal on the other side. Of course, such tests are not absolutely new, but previous papers (De Jong et al., 1981; Schramm et al., 1984) confined their attention to the anion structure, characterized by  $Q^n$  units. We will show that the condition postulated by Schramm et al. – namely, that at least 60% of the  $Q^n$  units must be preserved during the transformation from glass to crystal, – is not sufficient to predict the nucleation behaviour.

Generally, it has been observed that in many cases the coordination of the modifier cations by oxygen atoms show a higher degree of “regularity”, meaning a higher degree of uniformity of the bond distances, in glasses than in crystalline silicates. Obviously, there is competition between the local free energy which determines the short-range order in glass and the overall free energy of the formation of a long-range order. Therefore, the oxygen polyhedra around the modifier cations seem to be more “relaxed”, – meaning that bond distances and angles are more approximated to a local equilibrium configuration – in glass than in crystalline silicates where one can find locally energetically non-optimized coordination polyhedra without any regularity.

A particularly clear example is the crystal structure of albite ( $\text{NaAlSi}_3\text{O}_8$ ). Both phases (in all cases the original literature of the structures of crystalline silicates is cited by Liebau 1985) show an almost continuous sequence of Na – O distances (in nm):

l – T albite: 0.237 0.244 0.246 0.257 0.267 0.296 0.300 0.327 0.346;

h – T albite: 0.234 0.250 0.251 0.261 0.271 0.292 0.313 0.319 0.337.

An energy minimum for the sodium position is not well defined.

On the other hand, McKeown et al. (1985) found by EXAFS in glass of the albite composition Na – O distances ranging only from 0.256 nm to 0.262 nm and a coordination number of about 6!

This more regular oxygen environment of the sodium ion in albite glass is achieved by the oxygen atoms of six-membered rings of  $[\text{SiO}_4]$  tetrahedra (Taylor and Brown 1979) which are not compatible with the four-membered

rings of the crystalline feldspar structure of albite. Albite crystallizes only heterogeneously.

Also the further examples demonstrate that nucleation is obviously hindered, if the local more favourable coordination of the glass modifier cations is changed to form a crystalline long-range order.

Lippmaa et al. (1982) pointed out that the interpretation of a  $^{29}\text{Si}$  NMR study of glass and crystals of  $\text{PbO} \cdot \text{SiO}_2$  leads to the conclusion that the coordination of the lead ions by the oxygen atoms of  $[\text{SiO}_3]$  chains is more uniform in the lead silicate glass (only one slightly broadened signal) contrary to three separate lines of the alamosite where from the complicatedly folded "zwölfer single chains" (Liebau 1985) three different distances between  $\text{Pb}^{2+}$  ion and silica tetrahedra arise.

Greaves et al. (1981) found by EXAFS in the glass system  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  a sharply defined distance  $r(\text{Na}-\text{O}) = (0.230 \pm 0.003)$  nm and the coordination number  $\text{CN} = 5.0 \pm 0.5$ , whereas the  $\text{Na}^+$  coordination by oxygen atoms in the both crystalline phases is less regular (h-T  $\text{Na}_2[\text{Si}_2\text{O}_5]$ : five O atoms in the range of 0.229 to 0.239 nm, a further O atom at 0.260 nm; l-T  $\text{Na}_2[\text{Si}_2\text{O}_5]$ : two different  $\text{Na}^+$  sites with  $\text{CN} = 5$  (0.231 – 0.259 nm) and  $\text{CN} = 6$  (0.238 – 0.257 nm), respectively). These results are confirmed by the  $^{29}\text{Si}$  and  $^{23}\text{Na}$  NMR studies of Dupree et al. (1984), which reveal significant differences between the signals of glass and crystal.

There are also X-ray diffraction studies on  $\text{PbO} \cdot \text{SiO}_2$  (Imaoka et al., 1986) as well as of  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  (Imaoka et al., 1983). They demonstrate that in both cases the structures of the silicate anions of glass and the corresponding crystal are very similar: there are parts of chains in the lead silicate glass, and there are layer-like regions, consisting of six-membered rings, in the sodium disilicate glass. However, in spite of these similarities in the anion structures these glasses do not nucleate homogeneously. Therefore, we suppose that the changes in the cation coordination are responsible for the nucleation hindrance.

Also in glass of the diopside composition ( $\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$ ) the local gain of free energy leads to cation environments which are disadvantageous for the formation of a uniform long range order. Kirkpatrick et al. (1986) observed by  $^{17}\text{O}$  NMR that "wollastonite-like" and "enstatite-like" sites exist in the glass structure. It means that the optimal cation coordination needs parts of chains of different periodicities  $\text{P}:\text{P} = 2$  for  $\text{Mg}^{2+}$  like in enstatite and  $\text{P} = 3$  for  $\text{Ca}^{2+}$  like in wollastonite, in contrast to the energetic long range "compromise" of the diopside crystal of an uniform periodicity  $\text{P} = 2$ .

On the other hand, let us consider the glass structures of  $\text{Li}_2\text{O} \cdot \text{SiO}_2$  and  $\text{Na}_2\text{O} \cdot \text{SiO}_2$  (Yasui et al., 1983; Inone and Yasui, 1987) and of  $\text{CaO} \cdot \text{SiO}_2$  (Yin et al., 1986; Eckersley et al., 1988; Gaskell et al., 1991). In all three cases a very good comparability exists between the short range – and partially also the middle range – orders of glasses and corresponding

crystals in respect to anion structure as well as cation coordination. For instance, we will have a more detailed look on the  $\text{Ca}^{2+}$  coordination:

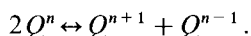
In the crystal structure, — we refer to wollastonite 2 M, the so-called parawollastonite, — three different Ca sites exist. Two of three sites have a coordination shell with six oxygen atoms within the range of 0.224 to 0.254 nm, whereas the third Ca site has a seventh oxygen atom in its shell at a distance of 0.264 nm. The  $^{17}\text{O}$  NMR spectra (Kirkpatrick et al., 1986) of wollastonite and  $\text{CaO} \cdot \text{SiO}_2$  glass are almost identical. The RDF, obtained by X-ray diffraction (Yin et al., 1986) indicates that  $\text{Ca}^{2+}$  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 (Eckersley et al., 1988), confirms the similarity between the Ca coordination shells in glass and wollastonite:  $r(\text{Ca}-\text{O}) = (0.237 \pm 0.012)$  nm and  $\text{CN} = 6.16 \pm 0.15$ .

These three chain silicates are able to crystallize homogeneously. Also, in the case of the other three homogeneously nucleating glass systems mentioned above, there are analogous structural similarities between glass and silicate crystal. The structure of lithium disilicate glass was investigated by X-ray diffraction (Aoki et al., 1986) and Raman spectroscopy (Iwamoto et al., 1983), and the barium disilicate glass by X-ray and neutron diffraction (Hasegawa and Yasui, 1987). In both systems a similar anion structure to the corresponding crystals are found: parts of strongly folded layers consisting of six-membered rings, which appear as so-called unbranched zweier single layers in the crystal structure. Also the cation coordinations are comparable with the corresponding crystal structure. The coordination number of  $\text{Li}^+$  is four in disilicate glass and crystal. The distance  $r(\text{Ba}-\text{O}) = 0.275$  nm is close to the distance  $\text{Ba}-\text{O}$  in sanbornite with an average value of 0.289 nm.

In contrast to the differences of the structures of glass and crystal in the feldspar system albite and the resulting difficulties to nucleate, Taylor and Brown (1979) found in a glass of the anorthite composition ( $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) a very good correspondence with the feldspar structure of  $\text{Ca}[\text{Al}_2\text{Si}_2\text{O}_8]$ . The four-membered rings needed for the crystal structure exist previously in glass, and also the coordination of  $\text{Ca}^{2+}$ , achieved by the oxygen atoms of these rings in glass corresponds very well to the coordination in anorthite: the RDF gives  $\text{Ca}-\text{O}$  distances within the range of 0.23 to 0.25 nm and a coordination number of about seven in the glass, whereas in the various crystalline modifications distances in the range from 0.231 to 0.271 nm are found. It means that the energetically favourable cation coordination in glass does not need to be changed essentially during nucleation. Therefore, the crystallization is promoted and homogeneous nucleation is observed.

In all the structures discussed so far we interpreted the nucleation behaviour by reason of structure similarities between glass and crystal. It means in the vocabulary of the theory mentioned at the beginning of our paper that  $W^*$  is small because of small values of the interfacial energy in the case of homogeneous nucleation.

However, another possibility to reduce the barrier to homogeneous nucleation exists additionally which promotes the nucleation by a decreasing of  $\Delta G_D$  and which depends also on the cation coordination. Stebbins (1988) observed by means of  $^{29}\text{Si}$  NMR of the systems  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  and  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  a higher content of  $Q^4$  groups in the lithium disilicate glass than in the sodium disilicate glass (which seems to contradict our thesis formulated above, because the corresponding crystal structures do not contain any  $Q^4$  unit, but only  $Q^3$  units!). Similar results are also reported by Schramm et al. and by Engelhardt and Michel. This may be interpreted in the form that the higher the so-called field strength (cation charge divided by the mean cation-oxygen distance) is, the strongerly a structural disproportionation of the dominant  $Q^n$  groups is possible which on its side is dependent on the thermal history of the glass:



Considering again the cation coordination, this phenomenon means that the cations of higher field strength partially achieve a more favourable coordination by elements of chains ( $Q^2$ ) instead of layers ( $Q^3$ ), which simultaneously leads to the formation of  $Q^4$  groups, too. The "mobility" of chain elements — we use this word in the meaning of "flexibility", "non-rigidity" of the structure elements, and not in the meaning of "diffusivity", since it is well known by e.g. the paper of Barklage-Hilgefort and Frischat (1980) that only single ions and not polyhedra diffuse, — is better than that of layer elements. In this way  $\Delta G_D$  can decrease and the nucleation can be promoted, if the stability of this local structure is not too high to form a long range order which needs the reversal process of the disproportionation. Obviously, this condition is fulfilled in the case of lithium disilicate.

But it is not fulfilled, for instance, in the case of calcium disilicate glass. Stebbins studied a glass of the composition  $40\text{CaO} \cdot 60\text{SiO}_2$  and found more than 6%  $Q^4$  groups in a system which should contain, theoretically, 66.7%,  $Q^3$  and 33.3%  $Q^2$ . It means the  $\text{Ca}^{2+}$  ions cause an additional disproportionation of  $Q^3$  units in order to enable more sites of the energetically more suitable coordination by chains. However, in the calcium disilicate system the formation of a long range order would lead to cation sites of coordination numbers less than six (Liebau 1985, p. 202). Therefore, the gain of overall free energy during the formation of a hypothetical long range order would not be sufficient to compensate for the local gain of free energy by the formation of chain structures. It means, the dispro-

portionalization process becomes irreversible and leads to the nucleation of two separate phases,  $\text{CaSiO}_3$  and  $\text{SiO}_2$ .

By comparing the fundamentally different nucleation behaviour of the systems  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ ,  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$  and  $\text{CaO} \cdot 2\text{SiO}_2$ , which show only small differences in their distributions of  $Q^n$  groups, the fundamental role of the cation coordination in respect to the nucleation is illustrated once more.

## Résumé

I. The coordination of the modifier cations may be more regular in glass than in the corresponding silicate crystal.

II. Homogeneous nucleation occurs preferentially if no drastic changes of the cation coordination (and also of the anion structure) are needed to build the crystal from the supercooled liquid and a relatively regular cation coordination is attainable in the crystal.

III. The coincidence alone of the amount of  $Q^n$  units between glass and crystal is not sufficient to explain the differences in nucleation, but it is also important to consider possible differences in the disproportionalization effects caused by the modifier cations.

IV. By such effects, structural units of higher mobility may result, which can promote nucleation, if the disproportionalization process is reversible.

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## References

- Aoki, N., Hasegawa, H., Yasui, I.: X-ray diffraction studies and molecular dynamics calculations of the structure of alkali disilicate glasses. *Yogyo-Kyokai-Shi* **94** (1986) 539–544.
- Barklage-Hilgefort, H. J., Frischat, G. H.: Reactions between  $\text{SiO}_2$  and  $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$  glass melts. *Phys. Chem. Glasses* **21** (1980) 212.
- De Jong, B. H. W. S., Keefer, K. D., Brown, G. E., Taylor, C. M.: Polymerization of silicate and aluminate tetrahedra in glasses, melts, and aqueous solutions. III *Geochim. Cosmochim. Acta* **45** (1981) 1291–1308.
- Dupree, R., Holland, D., McMillan, P. W., Pettifer, R.: The structure of soda-silica glasses: a MAS NMR study. *J. Non-Cryst. Solids* **68** (1984) 399–410.
- Eckersley, M. C., Gaskell, P. H., Barnes, A. C., Chieux, P.: The environment of Ca ions in silicate glasses. *J. Non-Cryst. Solids* **106** (1988) 132–136.
- Engelhardt, G., Michel, D.: *High-resolution solid-state NMR of silicates and zeolites*. Chichester New York Brisbane Toronto Singapore: John Wiley & Sons (1987), p. 200.
- Gaskell, P. H., Eckersley, M. C., Barnes, A. C., Chieux, P.: Medium-range order in the cation distribution of a calcium silicate glass. *Nature* **350** (1991) 675.
- Greaves, G. N., Fontaine, A., Largarde, P., Raoux, D., Gurman, S. J.: Local structure of silicate glasses. *Nature* **293** (1981) 611–616.

- Hasegawa, H., Yasui, I.: X-ray and neutron diffraction analysis of barium silicate glasses. *J. Non-Cryst. Solids* **95 & 96** (1987) 201–208.
- Imaoka, M., Hasegawa, H., Yasui, I.: X-ray diffraction study of the structure of silicate glasses. Part 2: Alkali disilicat glasses. *Phys. Chem. Glasses* **24** (1983) 72.
- Imaoka, M., Hasegawa, H., Yasui, I.: X-ray diffraction analysis on the structure of the glasses in the system  $\text{PbO} - \text{SiO}_2$ . *J. Non-Cryst. Solids* **85** (1986) 393–412.
- Inone, H., Yasui, I.: A molecular dynamics simulation of the structure of silicate glasses. *Phys. Chem. Glasses* **28** (1987) 63–69.
- Iwamoto, N., Umesaki, N., Dohi, K.: The structural analysis of  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass and melt by Raman spectroscopy. *J. Japan Inst. Met.* **47** (1983) 382–388.
- Kirkpatrick, R. J., Dunn, T., Schramm, S., Smith, K. A., Oestrik, R., Turner, G.: in *Structure and Bonding of Non-Crystalline Solids* (Eds: G. E. Walrafen and A. G. Revesz) Plenum Press (1986), pp. 303.
- Liebau, F.: *Structural Chemistry of silicates*. Berlin Heidelberg New York Tokyo Springer (1985).
- Lippmaa, E., Samoson, A., Mägi, M., Teeäär, J., Schraml, J., Götz, J.: High-resolution  $^{29}\text{Si}$  NMR study of the structure and devitrification of lead silicate glasses. *J. Non-Cryst. Solids* **50** (1982) 215–218.
- McKeown, D. C., Waychunas, G. A., Brown, G. E.: EXAFS study of the coordination environment of Al in a series of silica-rich glasses and selected minerals within the  $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  system. *J. Non-Cryst. Solids* **74** (1985) 325–348 and 349–371.
- Schramm, Ch. M., De Jong, B. H. W. S., Parziale, V. E.:  $^{29}\text{Si}$  Magic angle spinning NMR study on local silicium environments in amorphous and crystalline lithium silicate. *J. Am. Chem. Soc.* **106** (1984) 4396–4402.
- Stebbins, J. F.: Effects of temperature and composition on silicate glass structure and dynamics:  $^{29}\text{Si}$  NMR results. *J. Non-Cryst. Solids* **106** (1988) 359–369.
- Taylor, M., Brown, G.E.: Structure of minerals and glasses. Part 1: The feldspar glasses. *Geochim. Cosmochim. Acta* **43** (1979) 61–75.
- Turnbull, D., Fisher, J. C.: Rate of nucleation in condensed systems. *J. Chem. Phys.* **17** (1949) 71–73.
- Vogel, W.: *Glaschemie*. Leipzig: VEB Dtsch. Verlag f. Grundstoffindustrie (1983).
- Weinberg, M. C., Zanotto, E. D.: Re-examination of the temperature dependence of the classical nucleation rate: homogeneous crystal nucleation in glass. *J. Non-Cryst. Solids* **108** (1989) 99–108.
- Yasui, I., Hasegawa, H., Imaoka, M.: X-ray diffraction study of the structure of silicate glasses. Part I: Alkali metasilicate glasses. *Phys. Chem. Glasses* **24** (1983) 65–71.
- Yin, C. D., Okuno, M., Morikawa, H., Marumo, F., Yamahaka, T.: Structural analysis of  $\text{CaSiO}_3$  glasses by X-ray diffraction and Raman spectroscopy. *J. Non-Cryst. Solids* **80** (1986) 167–174.
- Zanotto, E. D., Weinberg, M. C.: Trends in homogeneous nucleation in oxide glasses. *Phys. Chem. Glasses* **30** (1989) 186–192.