Structural Changes in Two Different Types of Oxide Glass Melts: Borates and Metaphosphates

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X-ray diffraction experiments of molten oxide glasses, which give new insights into the structure of melts, were carried out. Using modern means (synchrotron radiation, image plates, container-less high-temperature technique) it could be shown that the short range order of melt and solid glass is often qualitatively different. If vitreous B_2O_3 or binary borate glasses with low content of network modifier are heated up above T_g, the network topology begins to alter. With rising temperature more and more of the boroxol groups are replaced by independent BO_3 groups. While melting a metaphosphate glass, however, structural changes of another kind take place. In solid glass the environment of the network modifier ions is similar to the one found in crystalline modifications, and their distances to the surrounding PO_4 tetrahedra have narrow distributions. In the melt, however, these distances scarcely become evident, probably owing to the increased thermal motion of the modifier ions.

Key words: X-ray Diffraction; Short Range Order; Borate Glasses; Phosphate Glasses; Glass Transition.

1. Introduction

In 1968 Riebling [1] formulated "The structure, or distributions of different polyhedral species, of an oxide melt and its corresponding glass are not very different." Twelve years later Waseda [2] stated "... with respect to the nearest-neighbor correlations, information from glassy samples is applicable to the molten state, as a first approximation." Both authors expressed what is the wide-spread opinion of the short range order (SRO) of glass melts.

Recently Gupta [3] has even tried to define "glass" by means of the equation

$$(\mathrm{SRO})_{\mathrm{solid}} = (\mathrm{SRO})_{\mathrm{melt}} .$$

This trial results in strengthening the commonly held opinion of melt structure. The equation seems to manifest that a glass and its melt always have the same SRO. Of course there is still another interpretation: $(\mathrm{SRO})_{\mathrm{melt}}$ refers only to the undercooled melt at a temperature higher than T_g but lower than $T_g + \Delta T$, where ΔT is a small positive quantity. If this view is taken, the equation makes a trivial statement because it is well-known that the glass structure is a frozen-in structure of the melt. If Gupta's equation has this meaning, nothing can be concluded about the melt structure at temperatures noticeably higher than T_g. The question arises, above what temperature the melt structure begins to differ from structure of the solid glass. Riebling gave information on this point [2]. He spoke of "an *exact* structural correlation between an oxide melt and its corresponding glass" which *sometimes* can be "limited to temperatures below $T_g + \Delta T$ (where $\Delta T \approx 300\,°\mathrm{C}$ to $400\,°\mathrm{C}$)". Please note that according to this author Gupta's equation should be fulfilled at least up to 300 K above T_g. Whether this is true or not, can be decided only by experiment.

What kind of structural changes can be expected if a glass is liquified by heating? The viscous flow is the main point in which solid glass and melt differ. Especially in case of a typical network glass (e.g. SiO_2 or B_2O_3) visualizing of the melting process is not so easy. In the vitreous state there is a very extended random continuous network, rigidly held together by strong Si-O or B-O bonds, respectively. With increasing temperature it is supposed that the network separates into network fragments, the size of which decreases with increasing temperature. This process is due to constitutional defects (broken bonds), the concentration of which increases with temperature. Topological defects (see [4–6]) are scarcely of importance [7]. In this respect it must be stated that the idea of constant fragments, being distinctly separated from each other and always made up of the same atoms, is certainly wrong. As pointed out by Krogh-Moe it is not necessary to postulate really unattached network pieces to account for a comparatively low viscosity [8]. It might be sufficient that accessible activated

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states exist and that in this way a flow process becomes possible.

As stressed by Krogh-Moe [8] the equilibrium concentration of the activated states is small, so that they themselves are not discernible in the radial distribution function. Even if a very extreme and unrealistic idea of network decomposing (a splitting into well separated pieces) has been accepted, it would be clear that the decomposing has no chance to be reflected in the radial distribution functions unless the pieces become extremely small. In other words: The SRO parameters are not influenced by network decomposing. It is rather a matter of medium range order (MRO). The well-known first sharp diffraction peak (FSDP) of the scattering curve has been regarded as a signature of MRO [9–10]. It can be expected that the decomposing has an effect on the scattering curve in the range $0.8\ \text{Å}^{-1} < s < 2\ \text{Å}^{-1}$ (where $s = 4\ \pi \sin \theta/\lambda$ and $2\ \theta$ = scattering angle, λ = wavelength). Indeed the experiments show that almost always the intensity at the left flank of the main peak and frequently its maximum intensity are increased as a result of remelting [11]. In detail, however, the particular kind of changes and their quantitative dependencies on the kind and the content of network modifier oxide are anything but easy to grasp.

2. Experimental

The diffraction experiments were performed using synchrotron radiation ($\lambda = 0.035$ nm) in the HASYLAB at DESY. A plane image plate serves as a detector, which is able to cope with high pulse rates. Both solid glasses and melts have been investigated by the same diffraction apparatus at virtually equal conditions (with regard to profile of primary beam, wavelength, form of the sample, kind of detection etc.). The container-less high-temperature technique, described in [12], has been used. It is especially suitable for common glass melts because it enables to achieve transmission geometry without parasitic scattering, and to apply high heating and cooling rates.

The glasses were prepared at the Otto-Schott-Institute in Jena. They were melted from analytical grade boric acid (H_3BO_3) and alkali carbonates at temperatures ranging from 1270 to 1450 K in platinum crucibles using an electrically heated furnace for about 30 minutes. After refining the melts were cast into graphite moulds and annealed, beginning from temperatures $T_g + 20$ K to 50 K with 7 to 10 K/min through the T_g region. The glasses were all analyzed by volumetric boron titration and flame spectroscopy of the alkalies. Because of their hygroscopic nature, they must be kept in a desiccator. The sample holder was loaded by pressing a rod-like piece of the glass into the slits of the preheated red-hot Pt-plate, in the course of which the glass becomes liquid. During this operation the temperatures ranges of nucleation and crystallization are speedily passed through. Afterwards the melt, held in the slits by surface tension, can be cooled down very slowly.

3. Results

The exposed image plates were scanned by the digitizing system of the Molecular Dynamics Company. The size of the pixels was 176 µm. Usually the data of 5 X-ray diagrams were averaged and then corrected for geometrical conditions, polarization absorption and background. The measurements cover the range $s \approx 0.6\ \text{Å}^{-1}$ up to $s_{\max} \approx 16\ \text{Å}^{-1}$. In order to suppress termination ripples the damping factor $[1 - \cos\{2\pi(s - s^*)/(s_{\max} - s^*)\}]$ was applied for $s > s^* = 10\ \text{Å}^{-1}$. The curves were normalized using the formalism after Norman and Krogh-Moe.

The results are presented in Figs. 1 to 5 in the form of the structure factor and the difference distribution function. The dashed curves refer to room temperature and the solid curves to high temperature.

4. Discussion

4.1. Vitreous B_2O_3 and Binary Borate Glasses with Low Network Modifier Content

Comparing the structure factor of vitreous B_2O_3 with that of molten B_2O_3 (see Fig. 1a) one is tempted to suppose that this material is a text book example of Riebling's view on melting. Apart from the main peak the two curves are almost identical, apparently indicating that the SRO of the melt is like the SRO of the glass. The radial distribution functions shown in previous publications [13, 14] seem to confirm this conclusion. The disintegration of the network seems to be the sole structural change, being expressed in a steady increase of the main peak and a steady shift to smaller scattering angles with rising temperature. However, this idea proves to be a misconception if distribution functions of adequate accuracy and resolution are ascertained. Then distinct alterations of the SRO due to melting are recognizable (see

Fig. 1b). In contrast to earlier publications, our difference distribution curve of vitreous B_2O_3 has distinct peaks at $r = 3.6$ Å and $r = 4.1$ Å, which are absent in the corresponding curve of molten B_2O_3 (Fig. 1b). As was emphasized by Williams and Elliott [15], the distances 2.74 Å and 4.11 Å are exclusively due to a boroxol ring. The disappearance of the peak at 4.1 Å gives us a first hint that boroxol groups, existing at room temperature, decay at higher temperatures. This would mean that with rising temperature the network not only disintegrates but also changes its topology.

For a closer examination we must consider the distribution of distances of possible structures. We restrict ourselves to a simple model of a random network of corner linked boroxol groups (without interconnecting BO_3 groups) and to a model which consists of 2-dimensional networks of independent BO_3 groups, as formerly advocated by Warren, Krutter, and Morningstar [16]. At present it is sufficient to concentrate on such details which can give rise to sharp peaks. So we can disregard distances between atoms of different 2-D-networks since such distances yield only "smeared" contributions due to the absence of defined correlations between the different networks. This is also valid for the distances between atoms of neighbouring boroxol rings, to a certain extent even in the case that the two are connected.

In this way we are restricted to distances which are relevant for our problem, the graphs of which are presented in Figure 6. To have a better comparability to the radial distribution functions, the numbers of distances are weighted by the atomic numbers of the contributing atoms. Figure 6a refers to the boroxol group. Figure 6b is based on a plane network of 26 BO_3 triangles, enclosing 5 hexagonal, 1 heptagonal and 2 pentagonal holes. Figure 6c, which is needed in the following, refers to a mixture of boroxol groups and tetraborate groups in the ratio 43 to 57. For this structure, dates of Hyman et al. [17] were used.

As can be seen, the distance of 4.1 Å, very frequent in the boroxol model, is hardly represented in the random network of BO_3 units. This distance is really a characteristic feature of the boroxol network. However, the distance of 2.7 Å, also emphasized in [15], is absolutely inappropriate as a characteristic of the boroxol group unless partial distribution functions are used. A distance of 2.74 Å is twice the shortest BO distance and consequently very frequent in the network after Warren, Krutter, and Morningstar. The peak at 2.7 Å in Fig. 6b solely corresponds to BB distances, whereas the peak at 2.7 Å in Fig. 6a represents BO distances. This peak is hardly suitable to decide for one of the two models. In addition, this small peak is so close to the strong OO peak at 2.37 Å that severe distortions due to the termination ripples are inevitable. The peak at 3.6 Å yields a better possibility. It is true that this distance exists both in the boroxol group and in the BO_3 network, but in Fig. 6a the corresponding peak rises much more above its environment than in Fig. 6b. Therefore the behaviour of the peaks at 4.1 Å and 3.6 Å together indicates that the solid glass contains a considerable amount of boroxol groups which then disappear in the melt.

When comparing the graph in Fig. 6b with the experiment it is obvious that the strong peak at 4.7 Å has only a very weak counterpart in the experimental distribution curve of the melt. One could suppose that this is a special feature of our model and easy to alter by choosing another ring statistic. The distance 4.75 Å is twice as big

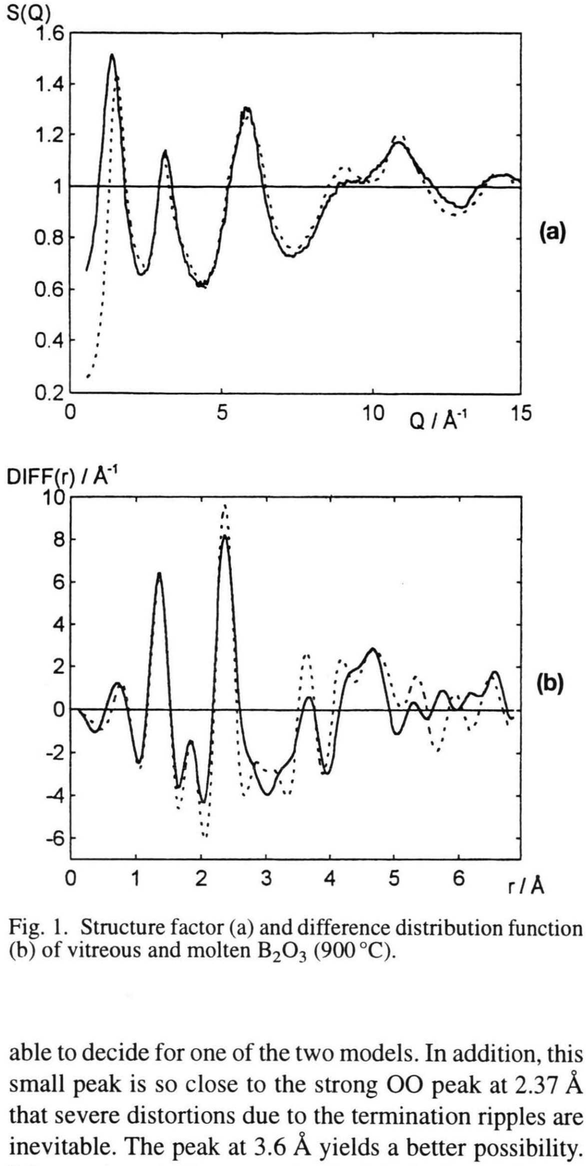

Fig. 1. Structure factor (a) and difference distribution function (b) of vitreous and molten B_2O_3 (900 °C).

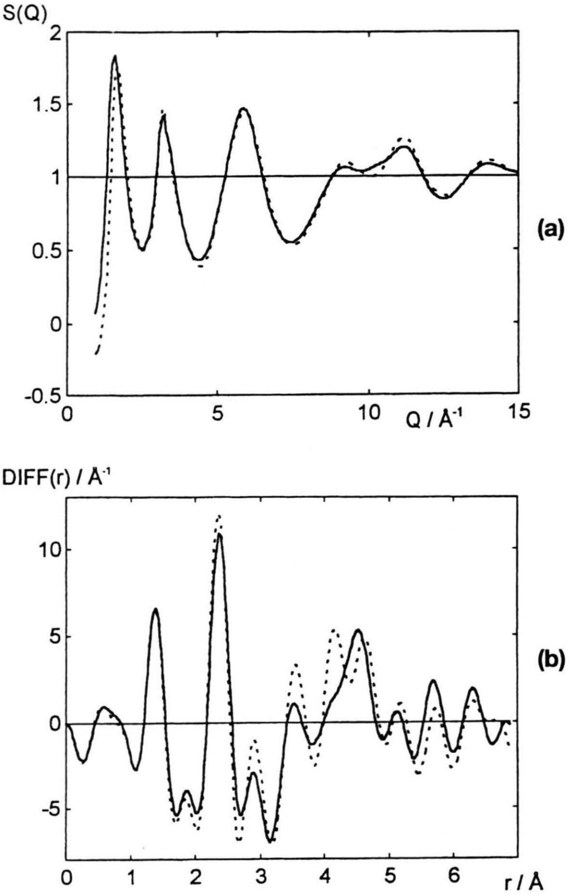

Fig. 2. Structure factor (a) and difference distribution function (b) of lithium borate glass, $15\,Li_2O \cdot 85\,B_2O_3$, and its melt at 900 °C.

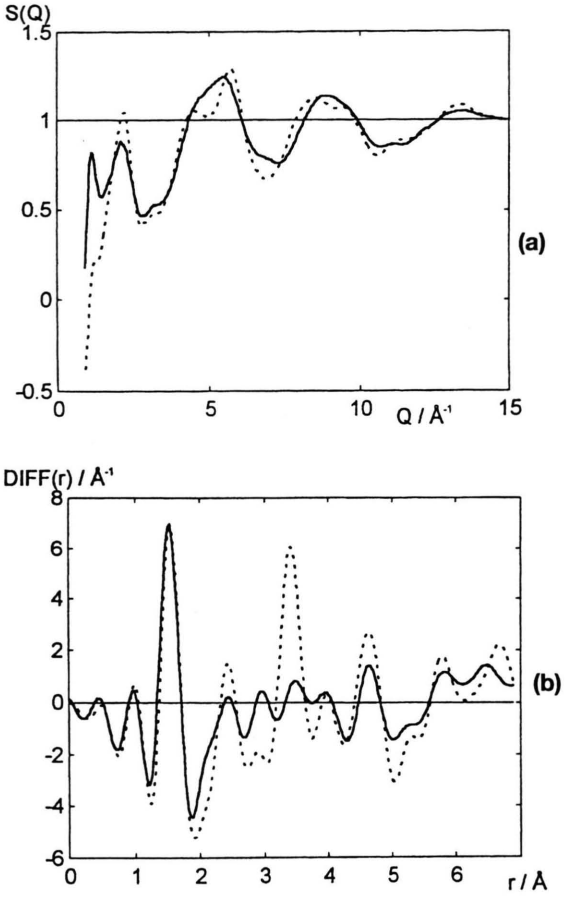

Fig. 3. Structure factor (a) and difference distribution function (b) of sodium metaphosphate glass, $NaPO_3$, and its melt at 770 °C.

as the side of a triangle and can be found if the BO bonds of two connected triangles form a straight angle. An alteration of the BOB angle within the plane of the network has only a negligible effect on this distance. If, e.g., a regular pentagon is enclosed by 5 triangles, the distance is shortened by 0.55%, or if 7 triangles enclose a regular heptagon, the reduction is 0.28%. These reductions are too small to produce a distinct change in Figure 6b. In other words, it is not to be expected that the peak at 4.7 Å in Fig. 3b can be noticeably decreased by choosing another ring statistic. Therefore it must be concluded that it is wrong to assume plane networks. Bigger variations can namely be attained if the connected triangles are not bound to the sample plane but are able to incline against one another or/and to twist around the BO bond. The stereoscopic pictures shown by Xu *et al.* [18] can give a good impression of the structure probably existing in the melt. Obviously the result of their molecular dynamics calculation is rather a model of molten than of solid B_2O_3. On that score we refer to Soules [19] who has pointed out that the simulated glasses have a higher fictive temperature than real glasses since the MD-runs are carried out only over a few hundred lattice vibrations.

As well-known, there are some objections to the boroxol ring model (see e.g. the detailed discussion by Johnson, Wright, and Sinclair [20]). Since we have the distribution functions both of the solid glass and the melt, we can confirm the view that at room temperature a number of the BO_3 triangles are part of boroxol rings. The network fragments in the melt, however, are built up by independent BO_3-triangles only. Obviously the activated states make the disintegration as well as the regrouping

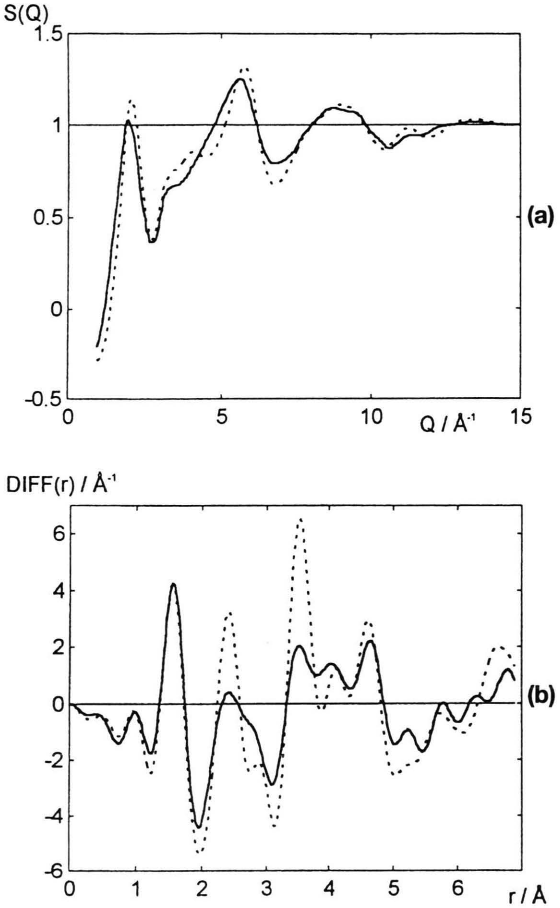

Fig. 4. Structure factor (a) and difference distribution function (b) of calcium metaphosphate glass, $Ca(PO_3)_2$, and its melt at 1200 °C.

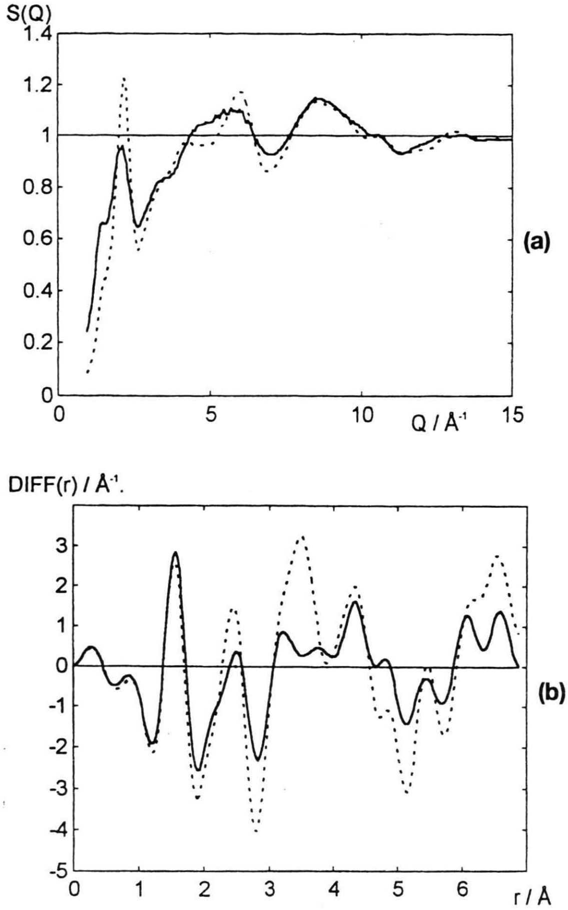

Fig. 5. Structure factor (a) and difference distribution function (b) of an invert glass, $20\,Na_2O \cdot 24\,MgO \cdot 25\,CaO \cdot 31\,P_2O_5$, and its melt at 1030 °C.

of the BO_3-units possible. Our result confirms findings of Strong [21] and is in accordance with the results of NMR measurements [22] and Raman studies [23, 24].

Binary borate glasses with a low content of modifier oxide show a very similar behaviour. Again the structure factors of melt and glass are distinguishable in the main peak only. It is shifted to lower scattering angles in the melt. The increase of its height, however, is much smaller than in the case of B_2O_3 and fails to appear if Li_2O is the modifier oxide (see Figure 2a). Again the distribution function of the melt is different from the distribution function of the glass (Figure 2b). Peaks at $r = 3.6$ Å and $r = 4.2$ Å are distinctly reduced in the melt. The frequency of sharply defined distances is given in Fig. 6c which is based on results achieved by Jellison and Bray [25]. According to these authors the network of the solid glass consists of boroxol groups and tetraborate groups, which probably exist in the proportion 43:57. Similar to B_2O_3 it must be concluded that the solid lithium borate glass is composed of complex groups whereas the melt is made of independent units.

At this point it should be emphasized that our measurements distinctly differ from previous ones with respect to the innermost coordination shell. In Zarzycki's or Misawa's radial distribution functions the BO peak and the OO peak broaden considerably with increasing temperature [13, 14]. In our distribution functions, however, the corresponding peaks are nearly unchanged in width. This is not only valid for B_2O_3 and borate glasses but also for most of the oxide glasses which we have studied. This means that the elementary structure units, the triangles or tetrahedrons, are hardly deformed in the

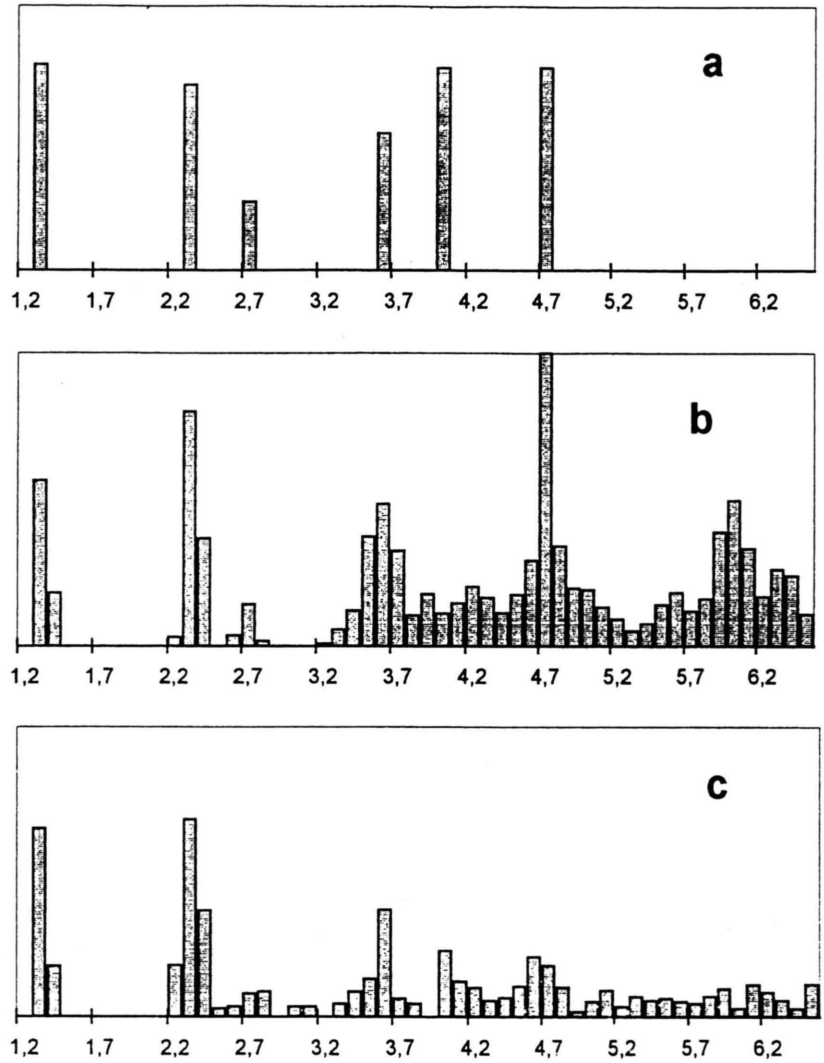

Fig. 6. Relative frequency of "well defined" distances a) in a boroxol group model, b) in a plane network of independent BO_3 groups, c) in a mixture of boroxol groups and tetraborate groups as a model for lithium borate glass with 15 mol% Li_2O. (The numbers of distances are weighted by the atomic numbers of the participating atoms.)

melt in spite of the much higher thermal motion. The elementary structure units prove to be very stable formations.

4.2. *Metaphosphate Glasses*

So far we have reported on typical network glasses, the extremes of which are SiO_2 or B_2O_3. With increasing content of modifier oxide the network becomes looser and looser. If the content reaches 50 mol%, the structural units form no longer a network but linear chains or rings. The transition from solid glass to viscous melt is much easier to imagine than in the case of a network glass.

As an example of a glass with chain-like structure first consider sodium metaphosphate glass. In this case already the structure factor (Fig. 3a) shows remarkable alterations with increasing temperature. One of them is the generation of a strong first sharp diffraction peak which grows out of a small shoulder at $s = 1.09$ Å^{-1} and is a result of changes of the MRO [26]. The other alteration occurs in that part of the scattering curve which is determined by the SRO. Two well separated diffraction maxima at $s = 4.0$ Å^{-1} and 5.6 Å^{-1} are replaced by one broad maximum when the glass becomes liquid. The most noticeable change in the difference distribution function is the nearly complete disappearance of a very high peak at 3.5 Å (Fig. 3b). This change is accompanied by a distinct lowering of the peak at $r = 2.4$ Å. Model-calculations by U. Hoppe have shown that the structure of the solid glass can be described as distorted versions of crystalline modifications of $NaPO_3$. Though the greatest resemblance can be obtained by a model based on Kurrol's salt, it must be admitted that the agreement is not strongly dependent on the choice of the crystalline modification. The model calculations show that the peak at 3.5 Å reflects Na-P and Na-Na distances. If one associates the peak at $r = 2.4$ Å with the edge lengths of the PO_4-tetrahedra, its behaviour seems to contradict the above given statement on the stability of the elementary structure units. However, this peak is the result of the superposition of O-O distances of 2.53 Å and of Na-O distances of 2.38 Å [27]. The whole picture becomes comprehensible if the behaviour of the peak at 3.6 Å is seen in connection with the behaviour of the peak at 2.4 Å. Obviously, as a result of the increased thermal motion, the sodium ions hold no longer firm sites between the phosphate chains. Therefore the contribution of the Na-O distances to the peak at 2.4 Å is reduced very much.

It should be mentioned that remelting the glass is no simple straight-forward process if the heating rate is low enough (e.g. 10 K/min). In this case tricyclophosphate crystallizes. Its structure is characterized by 3-membered rings of PO_4-tetrahedra. In comparison with this the tetrahedra form screw-shaped chains in Kurrol's salt. It is supposed that in the solid glass only 10% of the PO_4 tetrahedra exist in such rings [28]. Therefore crystallization involves structural reconstruction [29].

At higher temperatures all vibrational amplitudes are increased. However, as has already been said above, the mean P-O distance remains nearly unchanged. This is due to the fact that the strong, covalent P-O bond has a deep and narrow potential well. By contrast the potential curve of the weak, ionic Na-O interaction is very flat and asymmetric. Therefore the increased thermal energy leads to considerable elongations of the Na-O distances. In other words, the sodium ions occupy more space in the melt than in the solid glass, and the thermal expansion is in the first line due to the Na-O interactions and not to changes within the PO_4-tetrahedral chains. Most of the instantaneous Na-O distances in the melt are evidently larger than in the solid glass. Hence the scattering power density of the NaO_n polyhedra is decreased in the melt, and so their contrast to the phosphate chains is higher. The consequences for the scattering curves can be concluded, for example, from the fact that the neutron diffraction curve of KPO_3 glass has a high FSDP, whereas that of $NaPO_3$ glass has only a faint hint of a FSDP [30]. Since the potassium ion is larger than the sodium ion, while their scattering lengths are nearly equal, the scattering power density of the KO_n polyhedron is smaller than that of the NaO_n polyhedron. The higher contrast between the cavities of the modifier ions and the PO_4 chains makes the FSDP to increase. This is in accordance with general considerations of the origin and the behaviour of the FSDP [9, 10]. As the $NaPO_3$ melt produces a high FSDP in the X-ray scattering curve, we must conclude that the NaO_n polyhedra are increased in the melt. Indeed, model calculations by means of the Reverse Monte Carlo method have shown that the scattering curve and especially the FSDP of the $NaPO_3$ melt can be reproduced following the outlined conceptions [26].

After separating it by a fit procedure with Gaussian curves the FSDP has the position $s = 1.13$ Å^{-1} at room temperature and $s = 1.05$ Å^{-1} at 770 °C. In real space the corresponding features are damped sinusoidal waves with a wavelength of 5.6 Å at room temperature and 6.0 Å at 770 °C. Especially in the difference distribution function of the melt it is quite obvious that such a wave really exists [31]. (Unlike in Fig. 3b the abscissa must be extended up to 25 Å). The behaviour of the waves possibly reflects the increase of the mean distance of the polyhedra chains and the related increase of contrast between the chains and the NaO_n polyhedra.

Summarizing, it can be said that both the SRO parameters and the FSDP indicate that the melt structure differs from the glass structure in the dimensions of the NaO_n polyhedra. This must obviously result in another kind of embedding the NaO_n polyhedra in between the PO_4 tetrahedral chains. Probably the chains change their mutual mean distances and also their form by stretching. The result is a structure which has no resemblance to any crystalline form of sodium metaphosphate, as has been shown by our model calculations. Recently performed NMR- and Raman measurements support our conception concerning the neighbourhood of the network modifier ions. The increase in frequency of the ^{23}Na NMR peak and, to a lesser extent, the activation of the 490 cm^{-1} Raman peak at temperatures above T_g indicate that the predominant structural change involves the local bonding of the modifier ions [32].

The question arises if the changes, which have just been discussed, are typical of binary metaphosphate glasses or restricted to $NaPO_3$ only. Looking at the structure factors of calcium metaphosphate glass (Fig. 4a) one is tempted to suppose less drastic changes of the structure. The temperature-induced generation of a strong FSDP at $s = 1.09$ Å^{-1} does not appear. Even the starting point of the FSDP, the small shoulder in the structure factor of the solid glass, is missing. At higher s-values, however, an alteration is detectable, which corresponds to the alteration of the scattering curve of sodium metaphosphate glass. Indeed, the difference distribution functions of calcium metaphosphate show the same main difference in as much as the very high peak at $r = 3.6$ Å, found for the solid glass, is drastically lowered at higher temperatures. But also the behaviour of the PO-peak and the OO-peak is nearly the same as found in the distribution functions of sodium metaphosphate. The same structural changes seem to occur in both glasses. The non-appearance of the FSDP is no evidence of the contrary. Obviously the generation of a thermal-induced FSDP is a possible but not necessary reaction to such a kind of structural change. Whether the FSDP appears or not is a question of contrast and consequently depends on additional conditions (e.g. on the scattering amplitudes of the participating atoms).

It could be supposed that the structural change described here is restricted to metaphosphate glasses. Our experiments, however, show that also in the case of invert glasses the structural change due to melting is of the same character. An example is given in Fig. 5 which refers to an invert glass of about 30 mol% P_2O_5 and the oxides Na_2O, CaO and MgO, each with approx. 20 mol%. The most important fact is that the high 3.6 Å-peak of the difference distribution function vanishes in the melt. But also the behaviour of the main peak of the structure factor is noteworthy. At higher temperatures the peak dramatically decreases and a small thermal-induced prepeak grows at its flank.

5. Conclusions

The results reported here show that it is necessary to differentiate between several types of glass melts. In conformity with wide-spread ideas there is the possibility that in a large temperature range the melt and the solid glass have almost the same SRO. On the other hand, as demonstrated by our results, solidification, or vice versa, remelting is often connected with distinct alterations of the SRO. It seems reasonable to distinguish the following basic types of oxide glass melts:

1. Type I characterized by the fact that the mutual connection between the anion polyhedra remains unchanged in the course of melting and that the change of the network is mainly confined to the process of decomposing.
2. For type II the decomposing of the network is coupled with an alteration of its topology.
3. For type III it is essential that the spatial connections between modifier ions and surrounding anion polyhedra are distinctly changed during the melting process.

Type I should be called "Riebling's type" because it fully corresponds to Riebling's idea of melt structure. Perhaps vitreous silica belongs to this type. We must bear in mind, however, that for this glass T_g is very high and that the accuracy of the diffraction results, which have been obtained up to now, is still insufficient at the required temperatures. Concerning type II one should remember that for pure glass formers or glasses with a very small content of network modifying oxides, bond breaking and new tying represent the one and only way to change the SRO markedly. The structural change which is found in melts of type III might be the main way for glasses with higher content of modifier oxide. Bond breaking within the loose network or within the polyhedral chains or rings is relatively unimportant. In interaction with the network modifier ions, the polyhedral chains alter their shape (by straightening or puckering) or the space between themselves.

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