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The increased intensity of the first sharp diffraction peak of a NaPO₃ melt

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Abstract. The most striking change in the x-ray diffraction pattern of NaPO₃ glass which takes place during melting is the generation of a strong first sharp diffraction peak (FSDP). Starting from a model of KPO₃ glass and using reverse Monte Carlo simulations, the structure of molten NaPO₃ is approximated by replacing the K⁺ ions with Na⁺ ions and displacing them in a random manner within the extended cages originally occupied by the larger K⁺ ions. In this way the increased vibrations and the additional diffusive motion of the Na⁺ ions are taken into account. This motion requires considerably more room in the melt than is occupied by the cations in the glass. The model reproduces the structure factor of the melt, including the FSDP, and explains the disappearance of the peak at 0.35 nm in the total pair distribution function.

1. Introduction

According to the small width of the first maximum in the diffraction pattern of disordered systems this peak is suggested to be due to correlations in the medium-range order (MRO) [1–3]. The dependences on pressure, temperature, and composition of this part of the diffraction pattern are often observed to be quite different from those for other parts [2, 3]. For that reason, the peculiar first maximum in the diffraction pattern which is called the first sharp diffraction peak (FSDP) became a topic of investigation.

The most striking difference between the x-ray scattering intensity of the solid NaPO₃ glass and that of the melt is found in the early part of the intensity curve (see figure 1) [4]. The just-visible shoulder of the glass curve at $Q \cong 10 \text{ nm}^{-1}$ develops during melting to a strong FSDP. Q is the magnitude of the scattering vector ($= (4\pi/\lambda) \sin \theta$). Other, comparatively weak changes seem to result from a smoothing of the curve. In order to clarify the origin of the observations a study of the structural alterations between NaPO₃ glass and the melt is given in this paper. The technique applied in the diffraction experiments guarantees the measurement of the intensities without any contamination by container scattering [5].

Commonly, a glass structure is defined as a frozen configuration which is obtained from that of a supercooled liquid by a more or less quick cooling process. Thus, the structure of the sodium metaphosphate melt studied cannot be expected to be significantly altered from that of the glass at ambient temperature. With respect to small structural differences Gaskell [6] suggested that glasses need to be necessarily more ordered than the corresponding melt due to a reduction of the diffusive motion. Additionally, vibrational motion is also suppressed as a result of lower temperatures. The drastic changes in the x-ray diffraction curves observed for the NaPO₃ melt [4], in particular the enhanced FSDP

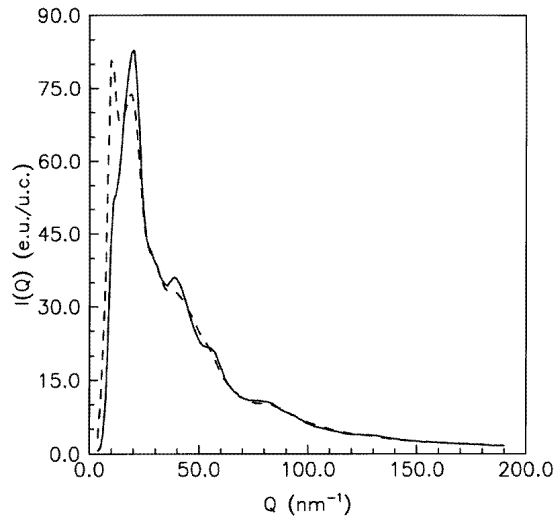


Figure 1. Intensity curves from x-ray diffraction measurements on NaPO_3 glass (the solid line) and the corresponding melt (the dashed line) [4]. Q is the magnitude of the scattering vector.

intensity, seem to contradict this view. This will be examined taking into account the specifics of the NaPO_3 system.

The known facts about the NaPO_3 glass structure should be listed, briefly. ^{31}P magic-angle spinning NMR [7], O (1s) x-ray photoelectron spectroscopy [8], and high-resolution neutron diffraction [9] have shown this glass to be made up of PO_4 tetrahedra linked by two of their corners. Presumably, the structural units form an entangled arrangement of chains with a few rings among them. The Na^+ cations are surrounded by on average five oxygen atoms [10]. The description of the MRO of such a glass, i.e. the detection of the structural origin of the FSDP, is a rather complex task. For some types of disordered material the first peak was proposed to be a quasi-Bragg reflection [1]. This peak can be associated with a quasi-periodicity in the MRO [2]. Gaskell (see [11]) sees a more general relationship between the first Bragg peaks of the related crystal structures and the FSDP position of the glass. Following this idea we would have to understand this peak as the result of an oriented, parallel packing of chain axes. From recent reverse Monte Carlo (RMC) simulations on the structure of KPO_3 glass [12] it became obvious that such a regular packing is not effective among the highly entangled chains in an alkali metaphosphate glass.

The clue to an explanation of the increase of the FSDP intensity was found by a comparison of the neutron structure factors of the glasses NaPO_3 and KPO_3 [13] (see figure 2). The structure factor of KPO_3 glass [14] has a high first peak at $Q_1 \cong 11 \text{ nm}^{-1}$ while the curve which corresponds to NaPO_3 glass [10] shows only a shoulder. Note that unlike the x-ray form factors for Na and K, the neutron scattering lengths of both sorts of atom are approximately equal. However, the first-neighbour distances r_{NaO} and r_{KO} have different values of 238 pm [10] and 275 pm [14], respectively. Hence, the space occupied by the larger K^+ cations results in a significantly lower scattering-power density compared to that of the Na^+ cations. The contrast between the phosphate chains and the KO_n polyhedra conglomerated as an interpenetrating substructure is increased. Consequently, the corresponding feature in the diffraction curve, the FSDP, is pronounced.

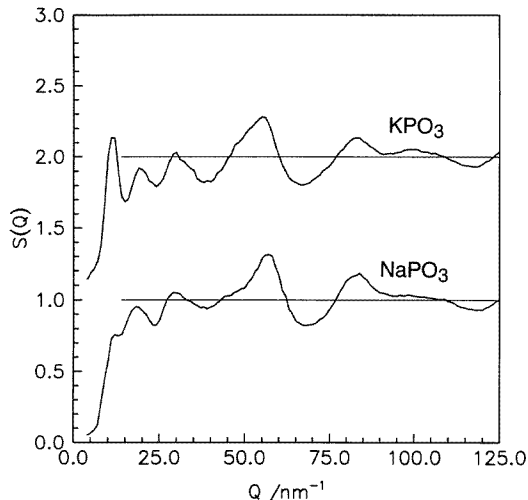


Figure 2. A comparison of the total Faber–Ziman structure factors of the glasses NaPO_3 [10] and KPO_3 [14] obtained from neutron scattering.

This explanation of the enhancement of the FSDP intensity for the melt was studied using models of NaPO_3 and KPO_3 glasses generated by the RMC method. The respective simulations were performed on the basis of neutron and x-ray diffraction curves. The RMC results for the KPO_3 system appear in a separate paper [12] while those for the NaPO_3 glass are not published.

2. Simulation of a structure for the NaPO_3 melt

2.1. The working hypothesis

The structural information obtained by diffraction methods corresponds to a snapshot of the instantaneous atomic positions. Thus, the atoms are seen at arbitrary positions of their vibrational movements. The number of broken P–O bonds in the melt at 1020 K should be very small. The breakage and formation of these bonds is assumed to be a continuous process. The PO_4 units which are also in the melt—mostly twofold linked—should form a flexible backbone. The sodium cations between the phosphate chains perform vibrations with large amplitudes. These modifier cations frequently change their sites.

All of the vibration amplitudes of bonds are increased according to the high temperature in the melt. But P–O and Na–O interaction potentials are quite different in nature. The strong, covalent P–O bond has a deep and narrow potential well while the comparably flat potential curve of the weak, ionic Na–O interaction is very asymmetric. In the NaPO_3 melt the energy level of the two types of vibration has risen likewise. This has different consequences for the bond lengths. The mean P–O distance is nearly unchanged while the mean Na–O distance is remarkably elongated. Hence, the spatial fraction in the melt structure which is occupied by the modifier cations is larger than that in the glass at ambient temperature. Most of the instantaneous Na–O distances are evidently larger than their equilibrium value. The mass density of the melt is diminished.

Starting from these ideas, the large cavities of the Na^+ cations in the NaPO_3 melt were

related to those of the K^+ cations in KPO_3 glass. In a first approximation the phosphate chains of these two systems were assumed to be of similar conformation. The Na^+ cations should be found displaced from the centres of the oversized cages. The exploitation of atomic models is required in order to simulate the corresponding simple alterations of the structure. In the present work models generated by the RMC method were used.

2.2. Generation of the model structures by reverse Monte Carlo simulations

The exploitation of models here generated by the RMC method makes it possible to avoid certain interpretations of the FSDP in the discussion of its behaviour observed via the x-ray intensities. For use in the simulations, reliable neutron and x-ray structure factors were available for the sodium and potassium metaphosphate glasses [10, 14]. The x-ray intensity curve of the $NaPO_3$ melt at 1020 K [4] is used in the comparisons.

The RMC procedures applied were in accordance to those described in references [15, 16]. In a separate paper about the structure of the KPO_3 glass [12], more details about the procedures were outlined. By means of a Metropolis Monte Carlo approach and using periodic boundary conditions the atomic configuration in the model box is changed step by step. The criterion of improvement is the agreement between the model structure factors and the corresponding experimental curves. The constraints used are given briefly: (a) the experimental x-ray and neutron structure factors, (b) minimal separation distances of the various pairs of atoms, and (c) maximal coordination numbers for the P and O atoms. Moreover, the maximal number of P–O–P bridges per PO_4 unit was 2. The formation of edge-sharing tetrahedra was suppressed. The RMC model of the $NaPO_3$ glass was generated in the same way. In the present paper it will only be used for comparisons. The number density of atoms in the $NaPO_3$ glass is 74 nm^{-3} . The corresponding value of 62 nm^{-3} for the other glass is much smaller.

Figures 3(a) and 3(b) show both sets of pair distribution functions, $g_{ij}(r)$. They represent averages of five configurations of 2000 atoms in each case. The first of the configurations used was the result after more than one million accepted steps in the simulations. The other four configurations were produced consecutively with about 100 000 further accepted steps between them.

In some of the resulting pair distributions of the $NaPO_3$ system, and in the O–O distribution of the KPO_3 system small peaks appear on the left-hand flank of the real first-neighbour distances. These minor peaks can be assumed to be artefacts. The obvious shortcomings in the simulations of $NaPO_3$ glass, however, have no influence on the considerations in the present paper. On the other hand, the splitting of the K–O peak is a real feature in the KPO_3 glass structure, as already discussed in reference [14].

In order to approach the structure of the $NaPO_3$ melt the following alterations were made starting from the final RMC configurations of the KPO_3 glass. (1) The K^+ cations were replaced by Na^+ cations. (2) Taking into account the smaller Na–O separation distance and the expected large vibration amplitudes, the sodium modifier cations were arbitrarily displaced through the large cages originally formed for the K^+ cations. During this procedure all of the P and O atoms remain in their positions. The resulting Na–O, Na–P and Na–Na pair distributions are plotted in figure 3(a) as dashed lines. The peaks were significantly flattened. Henceforth, the structural model of the $NaPO_3$ melt is represented by the three curves for the Na–O, Na–P and Na–Na pair distributions (dashed lines) and the three curves for the P–P, O–O and P–O distributions of the KPO_3 glass (solid lines) shown in figure 3(a).

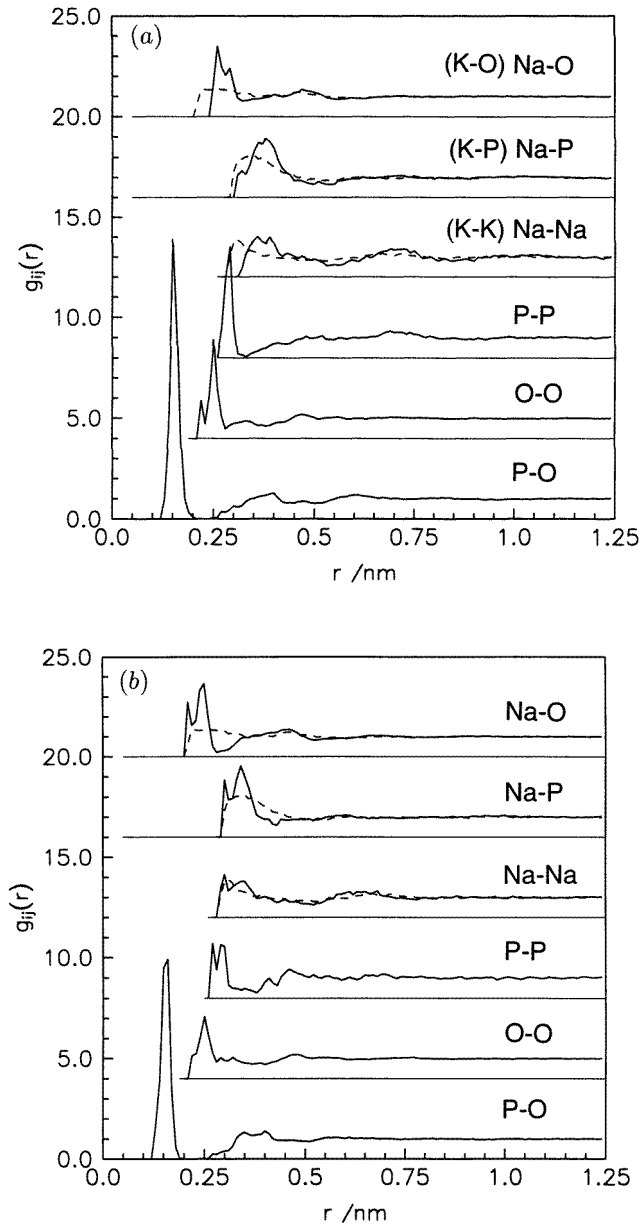


Figure 3. Pair distribution functions of the six atom pairs calculated from models of the NaPO_3 systems. Solid lines: the RMC model of KPO_3 glass as a starting point for the model of the NaPO_3 melt (a) and of NaPO_3 glass at ambient temperature (b). The dashed curves together with the P-P, O-O, and P-O curves plotted in (a) represent those distributions which relate to the final model of the NaPO_3 melt. For details of the modelling see the text.

3. Results

The differences between the models of the NaPO_3 melt and the NaPO_3 glass which concern the sodium environments are illustrated by the three upper curves of figure 3(b), where the

respective pair distribution functions of the melt, shown as dashed lines, are compared with the curves for NaPO₃ glass plotted as solid lines. The distribution functions of the melt appear more featureless. The first-neighbour peaks are much broader. Obviously, the mean values r_{NaO} and r_{NaP} are larger for the melt while the minimal separation distances are not changed.

As can be seen in a comparison of the three lower curves of figures 3(a) and 3(b), the P–O, O–O and P–P first-neighbour peaks in the RMC model of KPO₃ glass and, therefore, also in the model of the NaPO₃ melt are narrower than in the model of NaPO₃ glass. An alteration of these peaks was not the intention of our simulations of the melt structure. These changes do not affect the mean values of the first-neighbour distances and should not change the diffraction pattern much. However, further differences are obvious at larger distances. In particular, the broad peak in the P–P distribution function of the model of KPO₃ glass, i.e. the NaPO₃ melt, at about 0.70 nm is almost invisible in the model curve of the NaPO₃ glass. Due to its accentuated shape this peak was associated with P–P distances of neighbouring chains in KPO₃ glass [12]. Two reasons can be stated which might cause this pronounced P–P peak at 0.7 nm: (a) the distance between the axes of the phosphate chains is increased; (b) the chains are more stretched. Both effects can be caused by the large dimension of the K⁺ cations. In both cases this results in a gap without P positions between the chains. Thus, the P–P peak concerned reflects the interchain distance. No parallel packing of the phosphate chains is required.

To understand the consequences from changes in the chain packing for the scattering curves it might be useful to look at the partial structure factors. The respective curves of the models for the NaPO₃ melt and the NaPO₃ glass are shown in figures 4(a) and 4(b). The most noticeable difference is found in the P–P contribution. A clear first peak at 11 nm⁻¹ is found in the curve of the melt while only a shoulder is detected in the curve of the glass. This peak and others in the P–O, O–O, and Na–Na partial functions contribute to the enhanced FSDP intensity. Using equation (1) from reference [2] for the position of the principal peak of systems from dense-packed spheres, $Q_p \cong 7.7/r_1$ where r_1 is the mean first-neighbour distance, and taking into account the P–P distance peak at 0.70 nm, the FSDP position Q_1 can be related to a packing of PO₄ tetrahedra which do not belong to intrachain neighbours. On the other hand, in reference [12] it was suggested that Q_1 can correspond to a chain–chain distance of about 0.66 nm if a parallel packing of chains is assumed. One way or another, the enhanced FSDP intensity of the NaPO₃ melt can be related to a higher ordering of phosphate chains.

Wicks and McGreevy [17] have given the P–P, P–O, and O–O structure factors of a AgPO₃ glass, a system with a modifier cation of similar dimension to Na⁺. Their curves are quite similar to our results for the NaPO₃ glass. Hence, it is suggested that the alterations of the respective curves in the model of the NaPO₃ melt, i.e. the KPO₃ glass, are above all a consequence of the increased space occupied by the cations. Thus, the differences observed between the models of NaPO₃ glass and the melt express those modifications which they were intended to simulate. They result from increased Na–O distances.

Now total x-ray structure factors have been calculated according to the appropriate sum of the six partial functions shown in figures 4(a) and 4(b). In figure 5 these functions were compared with the experimental curves of NaPO₃ glass and the corresponding melt at 1020 K.

The $S(Q)$ -curve of the RMC model of the glass at ambient temperature shows a good agreement with the experimental result. The same agreement, not shown here, exists likewise with the neutron structure factor. This fact is simply attributable to the use of both functions as constraints in the RMC simulations.

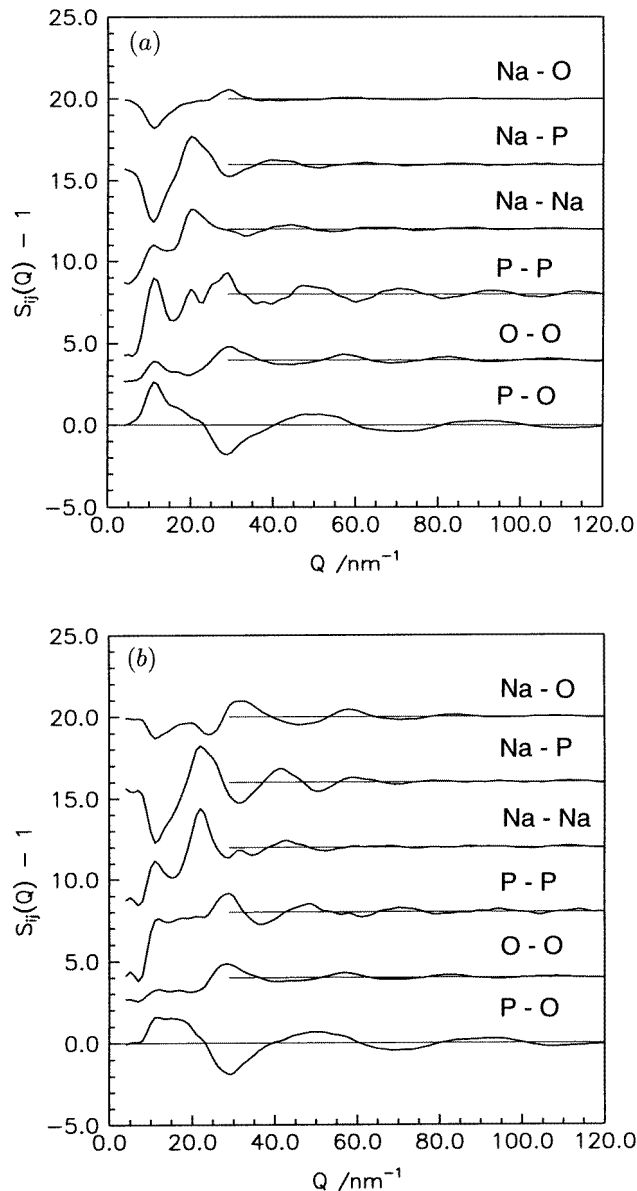


Figure 4. Partial structure factors of the six atom pairs calculated from models of the NaPO_3 systems. The partial functions shown correspond to the curves in figures 3(a) and 3(b). (a) Curves for the melt—thus, the functions of the Na-O, Na-P, and Na-Na pairs—correspond to the dashed curves in figure 3(a). (b) Curves for the glass.

As described in section 2, the model curve of the melt was obtained quite differently. The curve which is marked in figure 5 by a dashed line was calculated after step 1, the replacement of K^+ by Na^+ cations in the RMC model of the KPO_3 glass. From the analysis of the KPO_3 glass structure [12] it became obvious that the second peak at $Q_2 = 20 \text{ nm}^{-1}$ is caused by contributions from K-K and K-P pair correlations. This peak is still too high

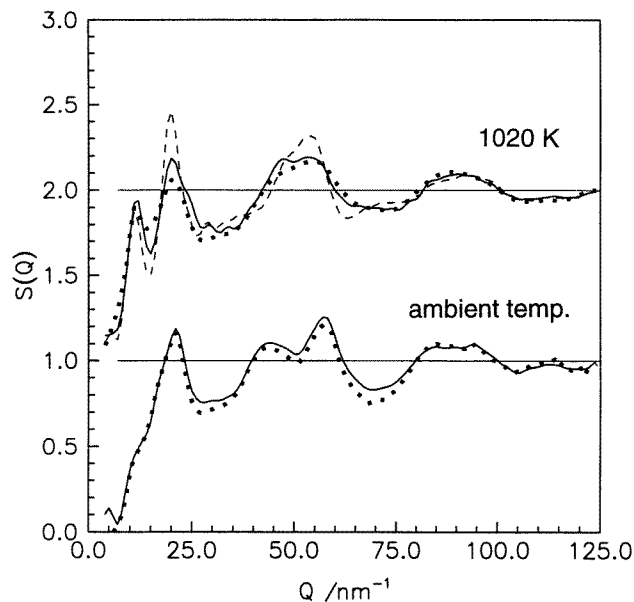


Figure 5. Total x-ray structure factors of the NaPO_3 systems at ambient temperature (glass) and at 1020 K (melt). The dotted lines denote the experimental curves. The curve for ambient temperature is compared with that of the RMC result for NaPO_3 glass (the solid line). The curve for the melt is compared with that for the RMC result for KPO_3 glass with K^+ cations simply replaced by Na^+ cations (the dashed line). This structural model modified by an arbitrary displacement of Na^+ cations in the extended cages yields the second curve (the solid line) which is compared with that of the melt as well.

compared with that in the experimental curve of the melt (the dotted line). The second step of the approach improves the fit by simply moving the sodium cations to arbitrary positions in the limits of the cages originally occupied by the large K^+ cations. Actually, the contributions to the peak at Q_2 were flattened. The experimental structure factor of the NaPO_3 melt is well reproduced by the final model structure factor (the solid line).

Finally, in order to make obvious the differences between the glass and the melt in the short-range order (SRO), total pair distributions were calculated from the $S(Q)$ -functions shown in figure 5 by Fourier transformation up to $Q_{\text{max}} = 155 \text{ nm}^{-1}$. The experimental $g(r)$ -functions are shown in figure 6 by dotted lines. The model curve from the RMC simulation of NaPO_3 glass fits the experimental result well. Both curves show definite distance peaks up to 0.5 nm. The pair distributions of the NaPO_3 melt are comparably smooth, except as regards the first peak at 0.155 nm which arises from the P–O bond. The large peak at 0.35 nm of the glass which arises from Na–P and Na–Na distances vanishes in the melt. The P–P peak at 0.30 nm of the model curve should be slightly broadened for better fitting the experimental result. On the whole, the SRO of the simple model on the basis of KPO_3 glass matches well with the melt structure.

4. Discussion

The NaPO_3 glass represents a polymer-like system rather than a 3D-network glass. A similar structure was assumed to be effective in the melt as well. At high temperature the

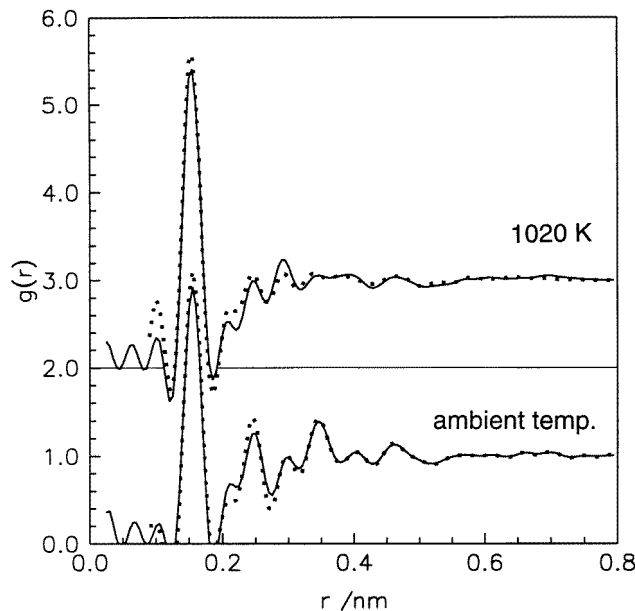


Figure 6. Total pair distributions of the NaPO_3 system at ambient temperature (glass) and at 1020 K (melt) calculated from the curves shown in figure 5 by Fourier transformation up to Q_{max} of 155 nm^{-1} . The dotted lines denote the experimental curves. The solid lines correspond to the respective model functions in figure 5.

weakly bonded Na^+ cations among the negatively charged, terminal oxygen atoms behave like in molten ionic salts whereas the phosphate chains can improve their conformation. These specifics are reflected for the melt by the sharp P–O distance peak and the flattened contributions which affect the sodium cations. The NaPO_3 system studied confirms the predictions from Salmon [3] about the temperature dependence of the FSDP intensity for partially covalent materials. The fraction of space which is occupied by the modifier cations increases with the temperature. Therefore, the contrast between the phosphate chains and the conglomerated oxygen polyhedra of the cations is increased with the FSDP intensity enhanced as well. This behaviour of the melt was shown in a straightforward manner using a model of KPO_3 glass where the replacement of K^+ with Na^+ cations and their subsequent displacement was sufficient to simulate the main features of the x-ray diffraction curve observed for the NaPO_3 melt.

The assumptions of Gaskell about a higher structural order in the glass compared with the corresponding melt [6] are also correct for the NaPO_3 system, but in a specific way. The local order around the Na^+ cations is essentially improved during freezing of the melt. Note, that the metal–oxygen coordination number in the model of KPO_3 glass was about 5.4 with a broad K–O distance peak [12]. This value is slightly reduced to about 5 in the model of NaPO_3 glass. The changes around the Na^+ cations affect the phosphate chains somewhat at the expense of their favourable conformation which is developed in the melt. This behaviour is also reflected by the width of the P–O distance peak (cf. figure 6). Though larger vibration amplitudes must be taken into account, this peak is even narrower in the melt.

The aim of the present work was to show by use of a simple model that the diffraction

curve of the NaPO_3 melt can be described by a structure which still preserves most of the building units found in the NaPO_3 glass. The basic structural elements like the NaO_5 polyhedra and the twofold-linked PO_4 tetrahedra are qualitatively the same in the melt and in the glass. The strongest alterations are associated with the weak Na–O interaction forces and consequently with increased mean Na–O distances at higher temperature. The structural changes in the MRO which concern the chain conformation reflected by the enhancement of the FSDP intensity are a consequence of this effect. From this latter point of view the NaPO_3 glass is significantly altered during melting. Its structure becomes more similar to the modified structure of the KPO_3 glass. However, it cannot be excluded that concerning certain details the melt structure is different from the modified structure of the KPO_3 glass.

The larger fraction of space occupied by the Na^+ cations can either lead to an increased separation distance of chains or to a stretching effect of chains. At first, a detailed comparison of this behaviour in the model of NaPO_3 glass with that in the model of KPO_3 glass should be made. From a rough impression, the chains appear more stretched in the latter system. At present, a direct study of the conformation of phosphate chains in the NaPO_3 melt is not possible. More information than from the x-ray diffraction curve alone is required.

The variety of time-independent equilibrium values of the P–O bond lengths seem to possess a narrower distribution in the melt than in the glass. This phenomenon was interpreted in the sense of the ‘relaxational’ effect of covalent bonds within the chains at higher temperature—which means in the melt—which was suggested by Salmon [3] for partially covalent systems. But this effect is superimposed on another one. Two P–O bond lengths, different by about 14 pm, were obtained for the bridging and the terminal oxygen atoms in alkali metaphosphate glasses [9, 14]. The behaviour of the two different P–O bonds in the PO_4 units with increasing temperature is not known. Thus, their contribution to the total width of the P–O distance peak of the NaPO_3 melt is not well understood.

It should be mentioned that during the heating of the glass, at about 700 K a transformation to the cyclo-triphosphate modification of NaPO_3 takes place [4]. This occurs above the transitional point T_g of about 550 K. NaPO_3 is stabilized as a glass by the entanglement of chains which should be formed in the melt. The temperature of 700 K determines approximately that range above which P–O bonds can be disrupted and a more global relaxation can take place. Below this temperature only a more local relaxation is possible.

It was an advantage of the simulations presented above that no assignment of the FSDP to certain structural elements was necessary. However, we would associate the position of the first diffraction peak with a frequently occurring distance between the chain axes whereby a parallel packing of the chains is not essential.

Acknowledgments

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References

- [1] Chechetkina E A 1993 *J. Phys.: Condens. Matter* **5** L527
- [2] Elliott S R 1995 *J. Non-Cryst. Solids* **182** 40
- [3] Salmon P S 1994 *Proc. R. Soc. A* **445** 351
- [4] Herms G, Hoppe U, Gerike W, Sakowski J and Weyer S 1995 *Proc. XVII Int. Congr. on Glass* vol 2 (Beijing: International Academic) pp 110–5

- [5] Herms G, Gerike W, Sakowski J and Weyer S 1996 *Meas. Sci. Technol.* **7** 627
- [6] Gaskell P H 1991 *Materials Science and Technology, A Comprehensive Treatment* vol 9, ed J Zarzycki (Weinheim: VCH) p 182
- [7] Brow R K, Phifer C C, Turner G L and Kirkpatrick R J 1991 *J. Am. Ceram. Soc.* **76** 1287
- [8] Gresch R, Müller-Warmuth W and Dutz H 1979 *J. Non-Cryst. Solids* **34** 127
- [9] Suzuki K and Ueno M 1985 *J. Physique Coll.* **46** C8 216
- [10] Hoppe U, Stachel D and Beyer D 1995 *Phys. Scr. T* **57** 122
- [11] Gaskell P H and Wallis D J 1996 *Phys. Rev. Lett.* **76** 66
- [12] Hoppe U, Walter G, Stachel D and Hannon A C 1996 *Ber. Bunsenges. Phys. Chem.* **100** 1569
- [13] Hoppe U and Herms G 1996 *Referate der 4. Jahrestagung der Deutschen Gesellschaft für Kristallographie; Z. Kristallogr. Suppl.* **11** 65
- [14] Hoppe U, Walter G, Stachel D and Hannon A C 1996 *Z. Naturf. a* **51** 179
- [15] McGreevy R L and Pusztai L 1988 *Mol. Simul.* **1** 359
- [16] McGreevy R L and Howe M A 1992 *Annu. Rev. Mater. Sci.* **22** 217
- [17] Wicks J D and McGreevy R L 1995 *J. Non-Cryst. Solids* **192+193** 23