Investigation of the Structures of Sodium Borophosphate Glasses by Reverse Monte Carlo Modeling to Examine the Origins of the Mixed Glass Former Effect

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Abstract
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Disciplines
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Comments
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ABSTRACT: We present new results for the Reverse Monte Carlo modeling of 0.35Na₂O + 0.65[xB₂O₃ + (1 − x)P₂O₅] glasses based on previously reported X-ray diffraction (XRD) data. Structural models have been generated that accurately reproduce the pair correlation functions and structure factors determined by XRD while maintaining nearly perfect charge neutrality between the positively charged cations and the negatively charged phosphate and borate oxyanion groups and while maintaining appropriate bond distances between the various atom pairs. These models, however, are not successful in accounting for the concentrations of network forming units (NFUs), as predicted by recent theoretical modeling and by magic-angle spinning nuclear magnetic resonance (MAS NMR) data for sodium borate glasses with similar stoichiometry. By a further refinement of the modeling, the NFU concentrations can be successfully reproduced as well. For the optimized structures, we investigate the question if the conductivity activation energy correlates with the volume fraction of the sodium long-range diffusion paths, as identified in the RMC modeling.

1. INTRODUCTION

Ion-conducting glasses are promising material systems for a large number of applications, such as rechargeable batteries, supercapacitors, and photochromic windows and mirrors because the cation mobility in these systems can be optimized over many orders of magnitudes by adjusting their chemical compositions. One way to increase (and decrease in some cases) the ionic conductivity is to use the so-called mixed glass former effect (MGFE).

The basic idea is to minimize the mismatch between the experimentally determined X-ray (XRD) or neutron (ND) diffraction total structure factor \( S(q) \) or the total radial distribution function \( G(r) \) of an \( n \)-species system and a test structure, which is iteratively optimized by a Monte Carlo procedure. \( S(q) \) is typically expressed as

\[
S(q) = \sum_{\alpha=1}^{n} \sum_{\beta=\alpha}^{n} \gamma_{\alpha\beta} (S_{\alpha\beta}(q) - 1)
\]

and \( G(r) \) is expressed as

\[
G(r) = \sum_{\alpha=1}^{n} \sum_{\beta=\alpha}^{n} \gamma_{\alpha\beta} G_{\alpha\beta}(r) - 1
\]

In the case of XRD, the weights \( \gamma_{\alpha\beta} \) in general depend on \( q \). Because \( G(r) \) is related by a Fourier transform to \( S(q) \), eq 2 would have a more complicated form. In the case of high-energy XRD, the \( q \) dependence can be neglected in first approximation, and a \( q \)-averaged value can be used instead; see ref 18.) In eqs 1 and 2 above, \( \gamma_{\alpha\beta} \) is a weighting factor for a pair of species \( \alpha \) and \( \beta \) that describes how strongly the partial structure factor \( S_{\alpha\beta}(q) \) or the partial distribution function \( g_{\alpha\beta}(r) \) affects the total structure factor. The weighting factors \( \gamma_{\alpha\beta} \) are given by

\[
\gamma_{\alpha\beta} = \frac{c_{\alpha} c_{\beta} f_{\alpha} f_{\beta}}{\sum_{\alpha} c_{\alpha} f_{\alpha}}
\]

where the \( c_{\alpha} \) are the concentrations of atoms of type \( \alpha \) and \( f_{\alpha} \) is the atomic form factors in the case of XRD and the bound

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coherent scattering lengths in ND. (As described above, \( \gamma_{\alpha \beta} \) depends, in general, on \( q \) in the case of XRD. The origin of this dependency is the \( q \) dependency of the atomic form factors \( f_\alpha(q) \).

The first XRD experiments with subsequent RMC modeling on alkali borophosphate glasses were reported in a recent paper by Le Roux et al.\(^1\) for the system 0.35Na\(_2\)O + 0.65[P\(_2\)O\(_5\)] with iterative substitution of P\(_2\)O\(_3\) for P\(_2\)O\(_5\). Starting from a configuration of pure sodium borate or sodium phosphate crystalline phases with iterative substitution of P\(_2\)O\(_3\) for P\(_2\)O\(_5\) (for B\(_2\)O\(_3\) on the borate rich side) and B\(_2\)O\(_3\) (for P\(_2\)O\(_3\) on the phosphate rich side) with subsequent adjustments to the correct stoichiometry, the authors of this article generated a glassy configuration and achieved a structure whose calculated \( S(q) \) and \( G(r) \) functions agreed well with the experimental values and further fulfilled the minimum distance constraints given in Table 1. In agreement with previous magic-angle spinning nuclear magnetic resonance (MAS NMR) data\(^3\) collected on a related system, 0.40Na\(_2\)O instead of 0.35Na\(_2\)O, their model also reproduced the finding that for small B\(_2\)O\(_3\) concentrations, B is predominantly in four-fold coordination with oxygen until the fraction of such tetrahedral borons saturates at \( \approx 43\% \) of all network forming units (NFUs), a value that can be rationalized by theoretical modeling.\(^2\)

However, the RMC modeling in ref 1 is not free of criticism. It is a well-known fact that the \( S(q) \) and \( G(r) \) functions do not have a unique relationship to the structure of the material giving rise to these functions.\(^{19-22}\) Structures generated by RMC modeling tend to be among the most disordered ones yet are still compatible with the experimental \( S(q) \) or \( G(r) \) functions and the given constraints. For these reasons, one should inform the RMC modeling with as much as possible further experimental or chemical information about the system. In the present case, the MAS NMR investigations\(^3\) and related theoretical modeling\(^2\) call for a more detailed consideration of coordinations and the charge neutrality between the positively charged mobile cations and the negatively charged borate and phosphate oxyanions.

Both of these considerations were not taken into account in the work of Le Roux et al.\(^1\) In particular, the concentrations of the various Q\(^{\alpha}\) species in their RMC models strongly violate the requirement of charge neutrality. A Q\(^{\alpha}\) species, \( Q = P \) or B, is an NFU with \( n \) bridging oxygens (bO\(_s\)); see Figure 1. A bO is shared by two Q\(^\alpha\) species and accordingly contributes a charge \(-1\) to each of them, whereas a nonbridging oxygen (nbO) contributes a charge \(-2\). With the oxidation numbers +3 and +5 for the boron and phosphorus atoms, respectively, the charges \( q_n \) can be expressed as \( q_n = n - 3 \) for the P\(^{\alpha}\) units (\( n = 0 \) to 4) and \( q_B = -\lfloor n - 3 \rfloor \) for the B\(^{\alpha}\) units (\( n = 2 \) to 4), cf. Figure 1. Note that to begin in consistency with ref 1, we initially include the P\(^{\alpha}\) unit in our modeling, model A, below, but show in our progressively more accurate models, models B and C, that the P\(^{\alpha}\) structure is not present in our structures, which is in agreement with all of the experimental studies of binary alkali phosphate glasses prepared at normal pressures.

The sum of all positive charges, Na\(^+\) ions and P\(^{\alpha}\) units, and negative charges, negatively charged Q\(^{\alpha}\) species, has to be zero. This constraint is violated in the RMC models in ref 1. For example, in the RMC structure generated for the pure sodium phosphate system, 0.35Na\(_2\)O + 0.65P\(_2\)O\(_5\), \( \approx 36\% \) more negative than positive charges were present. In addition, the Q\(^{\alpha}\) concentrations deviated from those predicted by theoretical modeling in ref 2, which succeeded to reproduce MAS NMR data\(^3\) for a sodium borophosphate glass series with the slightly different composition 0.4Na\(_2\)O + 0.6[P\(_2\)O\(_3\) + (1 - \( x \))P\(_2\)O\(_5\)]. It is noted that our more recent \(^1\)P MAS NMR measurements across all glasses for the glass series 0.35Na\(_2\)O + 0.65[P\(_2\)O\(_3\) + (1 - \( x \))P\(_2\)O\(_5\)] show good agreement with this theory. Moreover, B\(^{\alpha}\) units with 1, 2, 3, and even 4 nbOs were identified by Le Roux et al.,\(^1\) all of which have not been reported so far in all studies of alkali borate glasses. Furthermore, Le Roux et al.\(^1\) also reported the presence of large amounts of P\(^{\alpha}\) units in certain P\(_2\)O\(_5\) rich glasses, \( x \approx 1 \), when no such groups are known to exist in any phosphate glass produced at normal pressures.

These problems were the reason for improving the RMC modeling. In this new RMC study of these glasses, we take into account the charge neutrality and the concentrations of Q\(^{\alpha}\) species, and, in particular, address the following questions:

(i) Is it possible to generate RMC models that are charge neutral, contain B\(^{\alpha}\) units exclusively bonded to bO\(_s\), and are in good agreement with the XRD data?

(ii) Do these models give good agreement with the predicted concentrations of the various Q\(^{\alpha}\) species in these glasses from recent modeling studies? If not, is it possible to generate RMC models that are in good agreement with the measured Q\(^{\alpha}\) concentrations?

(iii) With access to this new modeling, are there new structural features that become available under these constraints? For example, can we learn more about the connectivity of the cation sites in these glasses?

Table 1. Distances of Closest Approach (Minimum Distances) Used in the RMC Modeling\(^a\)

<table>
<thead>
<tr>
<th>pair</th>
<th>P-P</th>
<th>P-B</th>
<th>P-O</th>
<th>P-Na</th>
<th>B-B</th>
<th>B-O</th>
<th>B-Na</th>
<th>O-O</th>
<th>O-Na</th>
<th>Na-Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>minimum distance (Å)</td>
<td>2.4</td>
<td>2.5</td>
<td>1.3</td>
<td>2.5</td>
<td>2.3</td>
<td>1.3</td>
<td>2.5</td>
<td>2.0</td>
<td>2.1</td>
<td>2.4</td>
</tr>
</tbody>
</table>

\(^a\) Distances involving O are for both nbO and bO.

Figure 1. Q\(^{\alpha}\) species considered for the borophosphate glasses of composition 0.35Na\(_2\)O + 0.65[xB\(_2\)O\(_3\) + (1 - \( x \))P\(_2\)O\(_5\)].
(iv) With access to the new and refined models of the structures, can we gain additional insight into the nature and type of the cationic environments and the alkali ion conduction pathways?

To answer these questions, we have improved the overall quality of the RMC modeling by adding new constraints in a stepwise manner.

2. RMC MODELING: GLOBAL CONSTRAINTS AND SIMULATION PROCEDURE

To identify the $Q^{(n)}$ species in a given structural RMC configuration, we have to specify in which cases an oxygen atom is considered to be connected to a boron or phosphorus atom. To this end, oxygen coordination shells between a minimum and maximum distance around a B and P atom are defined. The minimum distances are the distances of closest approach of oxygen atoms to B and P atoms allowed in the RMC modeling. These correspond to the onset of the first peaks in $G(r)$ for the binary sodium borate ($x = 1$) and phosphate ($x = 0$) glasses and are given in Table 1. The maximum distance is chosen to be 1.8 Å for both B and P and corresponds to the first minimum in $G(r)$ for the binary glasses. The mean P-O and B-O bond lengths refer to the maximum of the respective $G(r)$ functions within the coordination shells. The typical P-O bond distance in binary phosphate glasses is in the range of 1.5 to 1.6 Å. For borate glasses, the value for a B-O bond depends whether the B is three- or four-fold coordinated by oxygen. In the former case, the typical bond lengths lie between 1.3 to 1.4 Å, and in the latter they lie between 1.4 and 1.5 Å.

In our RMC modeling, we require that each phosphorus atom is coordinated to four oxygens, whereas a boron atom is coordinated to either three or four oxygens. An oxygen atom must be either one-fold coordinated, corresponding to an nbO, or two-fold coordinated, corresponding to a bO shared by two B, two P, or one B, and one P. These are our “global” coordination constraints. In addition, the minimum distances shown in Table 1 were applied. Except in the case of the O-O minimal distance, these are the same cutoff distances used in ref 1. (In former studies of Ag$_x$Na$_{1-x}$PO$_3$ glasses, the O-O minimum distance had to be set quite low, 2 Å, to improve the quality of the fit results. This fact was explained by the presence of additional water in the phosphate glass. In the present Article, we can exclude the presence of water because in the IR spectra the typical signatures for OH groups near 3000 cm$^{-1}$ are absent.)

The requirements of charge neutrality as well as the global coordination and minimum distance constraints, in connection with the information from $G(r)$ and $S(q)$, are not sufficient to provide structures where $B^{(4)}$ units are exclusively connected to bOs. To avoid the occurrence of such units, we further require all four-fold B atoms to be coordinated with only four bOs. To implement this further $B^{(4)}$ constraint in the RMC procedure, the oxygens are assigned to be either a bO or an nbO. The number $N_{nbO}$ of nbOs is given by (cf. Figures 1 and 2)

$$N_{nbO} = N_{P2} + 2N_{P2} + 3N_{P1} + 4N_{P0} + N_{B2}$$

Connecting this with the requirement of charge neutrality

$$N_{P2} + 2N_{P2} + 3N_{P0} + N_{B4} + N_{B2} - N_{P4} - N_{Na} = 0$$

leads, with $N_P = N_{P4} + N_{P3} + N_{P2} + N_{P1} + N_{P0}$ to

$$N_{nbO} = N_P + N_{Na} - N_{B4}$$

This means that $N_{nbO}$ is fixed once the number $N_{B4}$ of $B^{(4)}$ units is known. The complete dependence of the concentrations of all NFUs on the mixing-parameter $x$ was successfully modeled recently in ref 2. On the basis of these results, the number of $B^{(4)}$ can, to a good approximation, be written as

$$N_{B4} = \min[N_B, 0.43(N_B + N_P)]$$

where $N_B$ and $N_P$ are the total number of B and P atoms. From the $Q^{(0)}$ species distribution, it is moreover known that for $x < 1$, the three-fold coordinated boron atoms are exclusively connected to bOs as well. Accordingly, this constraint is also included in the modeling. For the RMC modeling at $x = 1$, the three-fold coordinated boron atoms are allowed to exhibit at most one nbO.

### Table 2. Weights $\gamma_{ab}$, See Equation 3, Calculated for the Composition 0.35Na$_2$O + 0.65[b$_2$O$_3$ + (1 – $x$)P$_2$O$_5$]$^a$

<table>
<thead>
<tr>
<th>$x$</th>
<th>0.0</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-P</td>
<td>0.121</td>
<td>0.092</td>
<td>0.063</td>
<td>0.035</td>
<td>0.011</td>
<td></td>
</tr>
<tr>
<td>P-B</td>
<td>0.015</td>
<td>0.028</td>
<td>0.035</td>
<td>0.030</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P-bO</td>
<td>0.159</td>
<td>0.176</td>
<td>0.182</td>
<td>0.153</td>
<td>0.097</td>
<td></td>
</tr>
<tr>
<td>P-nbO</td>
<td>0.199</td>
<td>0.140</td>
<td>0.083</td>
<td>0.047</td>
<td>0.018</td>
<td></td>
</tr>
<tr>
<td>P-Na</td>
<td>0.096</td>
<td>0.091</td>
<td>0.083</td>
<td>0.068</td>
<td>0.043</td>
<td></td>
</tr>
<tr>
<td>B-B</td>
<td>0.001</td>
<td>0.003</td>
<td>0.007</td>
<td>0.019</td>
<td>0.040</td>
<td></td>
</tr>
<tr>
<td>B-bO</td>
<td>0.015</td>
<td>0.041</td>
<td>0.077</td>
<td>0.129</td>
<td>0.211</td>
<td></td>
</tr>
<tr>
<td>B-nbO</td>
<td>0.012</td>
<td>0.018</td>
<td>0.023</td>
<td>0.024</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>B-Na</td>
<td>0.008</td>
<td>0.018</td>
<td>0.034</td>
<td>0.058</td>
<td>0.094</td>
<td></td>
</tr>
<tr>
<td>bO-bO</td>
<td>0.052</td>
<td>0.084</td>
<td>0.132</td>
<td>0.017</td>
<td>0.215</td>
<td></td>
</tr>
<tr>
<td>bO-nbO</td>
<td>0.131</td>
<td>0.133</td>
<td>0.120</td>
<td>0.010</td>
<td>0.080</td>
<td></td>
</tr>
<tr>
<td>bO-Na</td>
<td>0.063</td>
<td>0.087</td>
<td>0.120</td>
<td>0.150</td>
<td>0.192</td>
<td></td>
</tr>
<tr>
<td>nbO-nbO</td>
<td>0.082</td>
<td>0.053</td>
<td>0.027</td>
<td>0.016</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>nbO-Na</td>
<td>0.079</td>
<td>0.069</td>
<td>0.054</td>
<td>0.046</td>
<td>0.036</td>
<td></td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.019</td>
<td>0.023</td>
<td>0.027</td>
<td>0.034</td>
<td>0.043</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ In the calculations, the $f_{ab}$ from the NIST form factor table were taken.
In RMC modeling, the starting point is often a crystalline structure or a quasi-random structure, which satisfies the coordination constraints. Subsequently, the discrepancy between the measured and simulated total pair distribution function \(G(r)\) or the total structure factor \(S(q)\) is minimized by Monte Carlo moves of the particles. In this work, a slightly different approach was chosen to avoid any dependency of the finally arrived-at structure upon the starting atomic configurations. For models A and B (see below), RMC simulations for each composition were performed by starting from a random configuration of atoms (ions) in a box with a 10 to 20% lower particle density than that found experimentally. The optimized RMC structures were obtained by simultaneously adapting the density, coordinations, and charges to the required ones and by minimizing the cost function of the mismatch between experimental and simulated \(G(r)\) and \(S(q)\). The weights \(\gamma_{AB}\) needed for the determination of the simulated \(G(r)\) and \(S(q)\) were calculated from eq 3 and are listed in Table 2. The densities and total number of particles for the simulated structures of composition 0.35\(\text{Na}_2\text{O} + 0.65[\text{xB}_2\text{O}_3 + (1 - x)\text{P}_2\text{O}_5]\) are given in Table 3.

The box size adaptation was included because we are also interested in the nature and type of the second nearest neighbor coordinations, which could be heavily biased away from a fully random network structure or a fully crystalline structure. On the basis of MD simulations, it was shown\(^{19}\) that such starting configurations can lead to artifacts in the intermediate- to long-range length scales of the atomic structures. After good agreement between desired and obtained coordination constraints among the many atom pair coordinations was gained, the box size was iteratively decreased until the experimental densities were reached. Good agreement is considered to be achieved if >95% of the global coordinations are fulfilled, there exist in the final RMC structures a few boron and phosphorus atoms not satisfying these constraints. These are taken out from the analysis of the \(Q^{(n)}\) species distribution discussed below. To keep the right stoichiometry, a corresponding number of sodium ions is excluded from the analysis.

In the following, we will develop different RMC models by taking into account additional RMC constraints in a successive manner. In model A, we do not add any further information than described above, meaning that the model involves the following constraints: (i) the minimum distances given in Table 1, (ii) the charge neutrality, (iii) the global requirements on the coordinations, and (iv) the \(B^{(4)}\) constraints of all \(\text{bOs}\) and eq 7. The resulting RMC structures are then checked to see whether they can successfully reproduce the \(Q^{(n)}\) species distributions. Because this was not found to be the case, we include in model B the further constraint that a phosphorus atom can have either one or two \(\text{nbOs}\). This model successfully accounts for the \(Q^{(n)}\) species distributions, but in the resulting RMC structures, there is a significant fraction of the sodium ions that have no oxygens in their local environment. This unphysical feature is resolved with model C, where a minimum and a mean oxygen coordination number for the sodium ions are prescribed. In addition, we consider in model C the implications of known correlation effects between \(B^{(4)}\) units.

\[\begin{array}{|c|c|c|}
\hline
\text{x} & \rho_N \text{[Å}^{-3}\text{]} & N \\
\hline
0.00 & 0.072 & 5816 \\
0.20 & 0.077 & 5546 \\
0.40 & 0.082 & 5276 \\
0.60 & 0.083 & 5006 \\
0.80 & 0.088 & 4736 \\
1.00 & 0.092 & 4466 \\
\hline
\end{array}\]

* Densities agree with the values determined from experiments.\(^{13}\)

\[\begin{array}{|c|c|c|}
\hline
\text{x} & \text{model A} & \text{model B} & \text{model C} \\
\hline
0.0 & 0.97 & 1.00 & 0.98 \\
0.2 & 1.06 & 1.02 & 1.00 \\
0.4 & 1.05 & 1.01 & 0.99 \\
0.6 & 1.00 & 1.00 & 1.01 \\
0.8 & 0.99 & 1.00 & 1.01 \\
1.0 & 1.00 & 1.00 & 0.97 \\
\hline
\end{array}\]

* Value of one corresponds to perfect charge neutrality.
of P(4), P(1), and P(0) groups are taken to be zero in models B and C.

Data for model C are almost indistinguishable from those shown for model B. Note that the fractions of P(4), P(1), and P(0) groups are taken to be zero in models B and C.

Figure 4. Fraction of Q(4) species with respect to the overall amount of network forming units for models A (top) and B and C (bottom), symbols, in comparison with calculated values from the theoretical network forming units for models A (top) and B and C (bottom), developed in ref 2. Data for model C are almost indistinguishable from those shown for model B. Note that the fractions of P(4), P(1), and P(0) groups are taken to be zero in models B and C.

neutrality is also obeyed for the refined models B and C that are discussed further below.

However, the distribution of Q(4) species is not successfully accounted for by model A. As shown in Figure 4, there are significant deviations to the calculated values from the theory in ref 2, which succeeded reproducing MAS NMR data3 for a borophosphate glass series with the slightly different composition $0.4\text{Na}_2\text{O} + 0.6(\text{xB}_2\text{O}_3 + (1 - \text{x})\text{P}_2\text{O}_5)$. In particular, the P(2) fraction is much too low and, as described above, there are significant fractions of P(4) groups in all of the simulated glasses containing phosphorus that are not observed experimentally. Hence, a negative answer has to be given to the first part of question (ii) posed in the Introduction. This shows that the information content in S(q) distribution is not sufficient to predict such important feature as the Q(4) species distribution, which is essential for the formation of the network structure.

2.2. RMC Model B: Phosphate Groups Limited to P(2) and P(3) Groups. To account for the Q(4) species distribution, we extend model A by the additional constraint that the only charged phosphate units are P(2) units. Their number is $N_{P2} = N_{Na} - N_{B4}$ required by charge neutrality. According to the findings reported in ref 2, P(0), P(1), and P(4) units are absent for all glasses of the mixing-parameter x, where XRD data have been reported in ref 1. (Close to $x = 1$ (binary borate glass), the theory in ref 2 predicts also a few P(0) and P(1) units to appear in a narrow x interval. Preliminary MAS NMR results by some of us indeed give a fraction of $\sim 0.05$ of P(1) units at $x = 0.9$.) Hence, we can further set $N_{P2} = N_{P} - N_{P2}$. Figures 2 and 3 show that the S(q) and G(r) are again in excellent agreement with the experimental results. Moreover, the distribution of Q(4) species is now in good agreement with the expected one; see Figure 4. Hence, we can now give a positive answer also to question (ii) posed in the Introduction.

The successful modeling of the Q(4)-species distribution gives us some confidence that the simulated network structure resembles reasonably well the true structure, at least on the shorter length scales. However, this does not necessarily also imply that the local environments around the mobile sodium ions are well-described. Indeed, as shown in Figure 5, the oxygen coordination numbers of sodium in a spherical shell with radius 3 Å display unphysical features. For example, there occurs a significant number of sodium ions that are not coordinated by oxygens, and this amount becomes larger with increasing x. The mean coordination calculated from the histograms in Figure 5 yields values of $\sim 3$, which are clearly too small. It is to this last problem that we now turn.

2.3. RMC Model C: Consideration of Oxygen Coordination Around Sodium Ions. To solve the remaining problem of the proper oxygen coordination of the sodium ions, we include the following additional constraints:

- A sodium ion is coordinated by at least one oxygen atom.
- The average oxygen coordination number around sodium ions is set to 5.
- The average ratio of the numbers of nbOs to the number of bOs in the local coordination sphere is the same as in the whole system.

The second assumption is motivated by the fact that the mean oxygen about sodium coordination number for both sodium phosphate28,29 and borate30,31 glasses with comparable compositions was found to be close to 5. A coordination number between 4 and 6 was also reported for crystalline sodium borate and sodium phosphate systems.32 The last two constraints resemble the general idea of “local typicality”, which was recently suggested by Cliffe et al.16

As shown in Figures 2 and 3, excellent agreement with the experimental results of S(q) and G(r) can still be obtained when including these additional constraints. Also, the Q(4) species distribution from model C (not shown) is found to be almost indistinguishable from that of model B. The merit of model C is that the oxygen coordinations around the sodium ions now show a reasonable distribution. The coordination numbers scatter within a standard deviation of $\sim 2$ around the mean coordination 5 for each x value. For $x = 1$, this is consistent with previous RMC results of Swenson et al.33 for sodium borate glasses. The insensitivity of the standard deviation with respect to $x$ is a bit surprising because with replacement of borate by phosphate, nbOs are created, and these, due to their higher coordination...
fl exibility, could arrange more likely into coordinations corresponding to the preferred value 5.

The RMC structures of model C are in accordance with the scattering data from the XRD measurements and the knowledge about the distribution of Q(4) species, and they fulfill the commonly applied chemical constraints. We are thus able to address the question (iii) posed in the Introduction and are now therefore able to more accurately and reliably investigate additional structural features of the finally optimized structures.

3. BRIDGING OXYGEN CONNECTIVITY AND PARTIAL PAIR DISTRIBUTION FUNCTIONS

We first look at the connectivity between the different glass forming cations, that is, the fractions of bOs bonded to two boron atoms, two phosphorus atoms, and to one boron and one phosphorus atom. The results from model C, and used hereafter, are shown as open symbols in Figure 7. It is instructive to compare these data with those that would be obtained when the network-forming cations were connected randomly by the bOs. In this case, the probability for a bO to connect a X(n) with a Y(m) species (X, Y = B or P) is proportional to \( \alpha m n N_X m N_Y n \), where \( \alpha = 1/2 \) if both X = Y and \( m = n \), whereas \( \alpha = 1 \) otherwise. The bO fractions calculated from these probabilities are marked by the lines in Figure 7. The fact that the open symbols are close to these lines is, however, at variance with MAS NMR findings for the linkages reported in refs 3 and 34 for various stoichiometries of sodium borophosphate glasses. It is also not in agreement with basic considerations in the theoretical modeling presented in ref 2. In fact, to reason eq 7, it is important to take care that B(4) units do not like to become mutually linked. This tendency of avoidance of B(4)-B(4) linkages has been known for a sometime.22,35 The limiting case of complete avoidance of such linkages has been suggested by Beekenkamp35 to describe results for B(4) fractions in alkali borate glasses obtained from pioneering MAS NMR measurements.36 In ref 2, it was shown that this principle can also be applied to the alkali borophosphate glasses. It provides, therefore, a good basis for an acceptable approximate account of the Q(4) species distribution, whereas refinements are necessary for a more accurate description.

To study the consequences of the forbidden B(4)-B(4) linkages for our RMC structures, we have also implemented this constraint in the modeling. We find that this extension has almost no

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**Figure 6.** Fraction of sodium ions with the given oxygen coordination numbers in the RMC structures generated from model C.

**Figure 7.** Fraction of bOs connecting different network forming cations as a function of the mixing-parameter \( x \) for model C. The full/open symbols correspond to the models with/without forbidden B(4)-B(4) linkages. The solid lines mark the results in the case where the network forming cations would be randomly connected by the bOs. The dotted lines are guides to the eye connecting the data for forbidden B(4)-B(4) linkages.

**Figure 8.** Partial pair distribution functions for the pairs (a) B-B, (b) B-P, and (c) P-P. The dashed/solid lines correspond to the RMC models with/without forbidden B(4)-B(4) linkages.
The fraction of Q(4) borate units are of B(4) type, the partials become almost structureless in the case of forbidden B(4)-B(4) linkages. For the B-P linkages, the forbidden B(4)-B(4) linkages lead to a more pronounced first peak in the B-bO partial with (dashed line) forbidden B(4)-B(4) linkages. For the B-P partial, the forbidden B(4)-B(4) linkages lead to a more pronounced first peak at intermediate x values. The effect of forbidden B(4)-B(4) linkages shows up in a less pronounced second peak for larger x values.

Figure 9 shows the partial pair distribution functions for the pairs B-bO, B-nbO, P-bO, and P-nbO. The dashed/solid lines correspond to the RMC models with/without forbidden B(4)-B(4) linkages.

4. VOLUME FRACTION OF CONDUCTION PATHWAYS COMPARED TO THE ACTIVATION ENERGY

With the proper Na—O coordinations being taken care of, model C is at a level of description that allows us to address question (iv) posed in the Introduction, viz. that is to analyze the percolating accessible volume for the sodium ions. The accessible volume $V_{\text{acc}}$ is defined as the volume available to the cations for diffusive motion consistent with the constraints of the RMC modeling. To determine $V_{\text{acc}}$ from the RMC structures, all atoms of type X (X = B, P, O, and Na) are replaced by hard spheres with a given radius $r_X$. For sodium, $r_{\text{Na}} = 1.1$ Å is taken, which is close to the ionic radius of sodium. With the minimum distances $d_{X\text{Na}}$ listed in Table 1, we have to require $r_X = d_{X\text{Na}} - r_{\text{Na}}$, which fixes the hard sphere radii for X = B, P, and O. (It is important to note that these radii should not be misinterpreted as the real physical radii of the atoms but are rather chosen to be consistent with the RMC simulations.) The percolating accessible volume $V_{\text{acc,perc}}$ is that part of the accessible volume along which a sodium ion can move through the system (under the hard sphere constraints).

To determine $V_{\text{acc}}$ and $V_{\text{acc,perc}}$ from the finally arrived at RMC structures, all sodium ions are first removed from the system. Then, the simulation box is divided into a grid of $400 \times 400 \times 400$ cubic cells. By placing a test sodium ion successively into the centers of all of these cells, the minimum distance criteria are applied to decide whether the cells are accessible. The volume of all accessible cells is the accessible volume, $V_{\text{acc}}$. With the known set of accessible cells, the percolating cluster of neighboring accessible cells is determined by using the Hoshen–Kopelman
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The value of $F(x)$ around which the $F^{1/3}$ values scatter. The inset shows the variation of the conductivity activation energy for $0.35\text{Na}_2\text{O} + 0.65\text{xB}_2\text{O}_3 + (1-x)\text{P}_2\text{O}_5$ glasses. (The line is drawn as a guide to the eye.)

Figure 10. Cube root $F^{1/3}$ of the fraction of the percolating accessible volume for the sodium ions as a function of the mixing-parameter $x$. Squares/circles refer to the results calculated from the RMC model C without/with forbidden B(4)-B(4) linkages. The line marks the average value around which the $F^{1/3}$ values scatter. The inset shows the variation of the conductivity activation energy for $0.35\text{Na}_2\text{O} + 0.65\text{xB}_2\text{O}_3 + (1-x)\text{P}_2\text{O}_5$ glasses. (The line is drawn as a guide to the eye.)

Algorithm. The volume of this percolating cluster is the percolating accessible volume $V_{acc,perc}$. For binary alkali borate and phosphate glasses, a very interesting relation was proposed between the fraction $F = V_{acc,perc}/V$ of percolating accessible volume, $V$ being the total volume of the system, and the activation energy, $E_a$, of the ionic conductivity. This relation states that $E_a$ is a linear function of the cube root of $F^{1/3}$

$$E_a/k_B T = a - b F^{1/3}$$

where $a$ and $b$ are constants and $k_B T$ is the thermal energy of the system. (The constant $b$ was proposed to be proportional to the sixth root of the cation mass, but because only one type of mobile ion is present, this is not of relevance here.) It should be noted that in ref 38 $V_{acc}$ was determined by adding further constraints on bond valence sums to the hard sphere constraints. On the basis of MD simulations, it was shown, however, that $V_{acc}$ calculated in this way gives results comparable to those where the constraints on the bond valence sums are not included. We, therefore, refrain here from introducing bond valence sums in the present analysis.

Figure 10 shows that there is no significant dependence of $F^{1/3}$ on $x$ in the RMC structures of model C. This holds true for both the modeling with and without the constraint of forbidden B(4)-B(4) linkages. In contrast, the activation energy $E_a$, measured by some of us in the inset of Figure 10 first decreases rapidly when phosphate is replaced by borate and then runs through a shallow minimum around $x = 0.4$. It increases slightly at the end of the compositional range $0.5 < x \leq 1$. From the data on binary alkali borate and phosphate glasses reported in ref 38, the values $a \approx 51$ and $b \approx 81$ can be estimated for sodium ion conduction in binary sodium borate and sodium phosphate glasses. From these values of $a$ and $b$ for the binary glasses, one would expect $F^{1/3}$ to vary between 0.18 and 0.32 for the $E_a$ values shown in Figure 10 at room temperature. The higher $F^{1/3}$ calculated by us from the data here for the ternary sodium borophosphate glasses, $\sim 0.38$ to $\sim 0.46$, could be caused by the fact that we have deliberately not included additional constraints with respect to bond valence sums. However, the scatter in the $F^{1/3}$ data in Figure 10 is much smaller than the change 0.14 to 0.32. $E_a$ of $F^{1/3}$ expected from the analysis of the binary glasses in ref 38. Accordingly, one could conclude that the application of relation 8 to the RMC structures generated here may not be helpful in exploring the origin of the MGFE in alkali ion-conducting borophosphate glasses. It is possible that the inclusion of neutron scattering data in the RMC modeling can lead to improvements with respect to a possible correlation between $F$ and $E_a$. Incorporation of recent neutron scattering data on this same series of glasses is in progress and will be reported on in a future report.

5. CONCLUSIONS

Revisited investigations of the structures of $0.35\text{Na}_2\text{O} + 0.65\text{xB}_2\text{O}_3 + (1-x)\text{P}_2\text{O}_5$ glasses on the basis of RMC models have been carried out. The RMC models were generated by a further consideration of the XRD data reported in ref 1 using standard chemical constraints of bond distance and charge neutrality. It turned out that these were not sufficient to give satisfactory agreement with $Q^{(n)}$ species distributions as predicted by theoretical modeling and found by MAS NMR measurements for related glass compositions. By proper refinement of the modeling, RMC structures could be generated that are in agreement with both the XRD data and the $Q^{(n)}$ species distribution. Such refinements could also yield reasonable oxygen coordinations of the sodium ions. The fact known from MAS NMR findings that bOs are connecting network former cations in a correlated way was not automatically reproduced by the RMC models. It had to be enforced by taking into account the tendency of B(4) units not to become linked to each other. In this way, 3D RMC structures were generated for $0.35\text{Na}_2\text{O} + 0.65\text{xB}_2\text{O}_3 + (1-x)\text{P}_2\text{O}_5$ glasses, which reproduced well all currently available experimental information for this glass series.

Investigation of the percolating accessible volume for the sodium ions in the optimized RMC structures for different borate to phosphate mixing ratios points to the fact that there is no correlation between the percolating accessible volume and the conductivity activation energy across all mixing ratios of these glasses. Because it was shown by some of us that the additional consideration of neutron scattering data can significantly improve the quality of the RMC generated structures, it is worthwhile to include this further information in the future and to check whether the absence of significant correlations between the percolating accessible volume and the activation energy remains. The lack of these correlations in the present modeling suggests that other routes should be followed to explore the origin of the occurrence of the MGFE in alkali borophosphate glasses. Indeed, recent studies by some of us suggest that Coulomb trapping effects of the charges associated with various glass-forming units are playing the decisive role for understanding the MGFE in this system. A further step for gaining deeper microscopic insight into the origin of the MGFE could be a combination of the RMC method with a kinetic Monte Carlo approach. Such studies are in progress.

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