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A29 Abstracts
Packing in alkali and alkaline earth borosilicate glass systems

Saurav Bista, Anthony O’Donovan-Zavada, Tyler Mullenbach, Maranda Franke, Mario Affatigato & Steve Feller*

Physics Department, Coe College, 1220 First Avenue NE, Cedar Rapids, IA 52402, USA.

Manuscript received 18 August 2008
Revised version received 21 December 2008
Accepted 12 January 2009

Packing fraction is defined as the ratio of ionic volume to molar volume, and is a useful parameter for analysing structural changes with composition. Alkali borosilicate glasses, RM,O,B₂O₃,KSiO₂ (M=Li, Na, K, Rb or Cs), were studied using fixed K while varying R. This was done for several suitable K values for each alkali used. Packing fractions were determined using experimental density data and Shannon radii, and were then compared with the packing fractions for binary borate and silicate alkali glasses. Further, two alkaline earth borosilicate glass families, RMO,B₂O₃,KSiO₂ (M=Ca or Ba), were studied and the packing fractions were also compared with the packing fractions for binary borate and silicate alkali glasses. Alkali ions having volumes larger than oxygen (K, Rb and Cs) dominate the packing at all K values; we define this as ionic packing. For alkalis smaller than oxygen (Li and Na), the packing is controlled by the covalent oxygen network (borate and silicate units); this is defined as covalent packing. The alkaline earth borosilicates (RCaO,B₂O₃,KSiO₂ and RBaO,B₂O₃,KSiO₂) have packing that is intermediate between the ionic and covalent packing trends of the alkali borosilicate systems.

1. Introduction

In our previous work we used the packing fraction to describe the structure of binary alkali and alkaline earth oxide glasses(1,2) and observed three different packing trends. Ionic packing trends were found for ions much greater in size than that of oxygen (K, Rb, and Cs). These trends were marked by monotonic rises in packing fraction followed by an asymptotic approach to the packing fraction for a dense random packing of equally sized hard spheres, 0.64. Another trend, covalent packing, was observed for ions smaller than oxygen (Li and Na), where structural changes in the oxide network (i.e. borate and silicate short range units) dominated the packing. The packing trends of alkaline-earth glasses were intermediate between the ionic and covalent trends.

In this paper we analyse the packing fractions from alkali and alkaline earth borosilicate glasses and compare them to previous binary systems. As before, we have chosen Shannon radii and diffraction data,(3–7) adjusted for the coordination number of the ions in crystals, for calculating the ionic volume. Table 1 lists the relevant radii, coordination, ionic volume, and estimated uncertainties for each ion used in the packing calculation.

2. Calculation of packing fractions

The packing fraction (PF) is given by

$$PF = \frac{4}{3} \pi \sum \frac{r_i^3 N_i}{V_f}$$  \(1\)

where the i-summation is taken over the elements in the formula unit, \(r_i\) and \(N_i\) are the radii and number of each ion per formula unit, and \(V_f\) is the volume of a formula unit of glass. \(V_f\) is found by the ratio of the mass of the formula unit to the density of the glass. Density data used in this study were taken from the literature.(8–15)

3. The Dell, Bray, and Xiao structural model

The Shannon radii that we used to calculate the ionic volume are different for three or four-coordinated boron. Modified borosilicate glasses share added oxygen to form two glass subnetworks: borate and

Table 1. Ion coordination, radii, and volumes(1–7)

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Ba</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>O</th>
<th>Si</th>
<th>M₃B</th>
<th>M₄B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coordination</td>
<td>7-8</td>
<td>9</td>
<td>4</td>
<td>6</td>
<td>8</td>
<td>9</td>
<td>10</td>
<td>2</td>
<td>4</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Radius (Å)</td>
<td>1.23</td>
<td>1.61</td>
<td>0.73</td>
<td>1.16</td>
<td>1.65</td>
<td>1.77</td>
<td>1.95</td>
<td>1.21</td>
<td>0.4</td>
<td>0.15</td>
<td>0.25</td>
</tr>
<tr>
<td>Radial uncertainty (Å)</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>7.80</td>
<td>17.48</td>
<td>1.63</td>
<td>6.54</td>
<td>14.71</td>
<td>19.16</td>
<td>31.06</td>
<td>7.42</td>
<td>0.25</td>
<td>0.01</td>
<td>0.07</td>
</tr>
<tr>
<td>Volume uncertainty(Å³)</td>
<td>0.95</td>
<td>1.63</td>
<td>0.34</td>
<td>0.51</td>
<td>0.6</td>
<td>0.8</td>
<td>1.0</td>
<td>0.37</td>
<td>0.02</td>
<td>0.003</td>
<td>0.008</td>
</tr>
<tr>
<td>Fractional volume uncertainty</td>
<td>0.12</td>
<td>0.09</td>
<td>0.21</td>
<td>0.08</td>
<td>0.04</td>
<td>0.04</td>
<td>0.03</td>
<td>0.05</td>
<td>0.08</td>
<td>0.3</td>
<td>0.11</td>
</tr>
</tbody>
</table>

*Corresponding author. Email SFELLER@coe.edu
silicate. The sharing is model dependent. In this paper, we use “silicate” and “borate” to indicate these subnetworks. The Dell model\(^{(16)}\) was used to find the fractions of three (\(N_3\)) and four (\(N_4\)) coordinated boron in each glass since the boron radius is dependent on coordination.

The glass composition is \(R\)\(M_2O\).\(B_2O_3\).\(K\)\(SiO_2\) for alkali borosilicate glasses and \(R\)\(MO\).\(B_2O_3\).\(K\)\(SiO_2\) for alkaline earth borosilicate glasses. The Dell model gives the \(N_4\) fraction as a function of \(R\)\(^{(11)}\)\(^{(16)}\) according to in Equations 2(a,b) through 4(a,b)

For \(0\leq R\leq R_{max}\) (where \(R_{max}=1/2+K/16\))

\[
N_4 = R \tag{2}
\]

For \(R_{max}\leq R\leq R_{d1}\) (where \(R_{d1}=1/2+K/4\))

\[
N_4 = R_{max} \tag{3}
\]

For \(R_{d1}\leq R\leq R_{d3}\) (where \(R_{d3}=2+K\))

\[
N_4 = \frac{8+K}{12} \cdot \frac{R}{24+12K} \tag{4}
\]

For all values of \(R\)

\[
N_3 = 1 - N_4 \tag{5}
\]

The PF for borosilicate glasses was calculated by using Equation (1), together with Equations (2) to (5) for the Dell model, to take into account the effect of coordination on the boron radius.

Table 2. Density and packing of alkali and alkaline earth oxides\(^{(17)}\)

<table>
<thead>
<tr>
<th>(Li_2O)</th>
<th>(Na_2O)</th>
<th>(K_2O)</th>
<th>(Rb_2O)</th>
<th>(Cs_2O)</th>
<th>(CaO)</th>
<th>(BaO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm(^3))</td>
<td>2.013</td>
<td>2.27</td>
<td>2.35</td>
<td>4.0</td>
<td>4.65</td>
<td>3.34</td>
</tr>
<tr>
<td>PF</td>
<td>0.43</td>
<td>0.45</td>
<td>0.68</td>
<td>0.69</td>
<td>0.69</td>
<td>0.54</td>
</tr>
<tr>
<td>Structure</td>
<td>cubic</td>
<td>amorphous</td>
<td>cubic</td>
<td>cubic</td>
<td>hexagonal</td>
<td>cubic</td>
</tr>
</tbody>
</table>

As with binary alkali borate glasses,\(^{(11)}\) we observe that packing in alkali borosilicate glass systems follows two general trends, see Figure 1. Glasses with modifying ions larger than oxygen (K, Rb and Cs) follow ionic packing as defined earlier, and glasses with ions smaller than oxygen (Li and Na) exhibit covalent packing controlled by the borate and the silicate structural changes. The packing fraction was plotted against the molar fraction of alkali oxide, which is denoted by \(X\)

\[
X = \frac{R}{R+K+1} \tag{6}
\]

Figure 1 and Table 2 show the PFs of the respective metal oxides. In general, as \(X\) approaches 1, the PF of the glass approaches that of the corresponding metal oxide.

In the lithium borosilicate glasses, as \(K\) decreases the PF displays more pronounced maxima, indicative of changes in the borate structure and the formation of tetrahedral borons.\(^{(16)}\) We note that the packing curve of the lithium silicate glasses demonstrates a monotonic rise with the addition of alkali oxide (Figure 2). This happens as there is no coordination change in silicon; it remains tetrahedral with the addition of alkali oxide. What we observe in Figure 2 is that the PF roughly follows the prediction of the Dell model, where added alkali initially associates principally with the borate part of the glass structure.
and the PF is close to the binary borate value. The $K=1$ and 0·5 systems follow the $K=0$ binary borate glass curve until about $X=0·2$ and 0·25, respectively, where they diverge from the binary curve. The $K=3$ system only forms glass for $X \geq 0·2$ and already has deviated from the binary borate glass curve. At higher lithia contents, all systems converge near the packing fraction, 0·43, of lithium oxide ($X=1$).

Figure 3 shows a detailed plot of the PF data for the $K=1$ and binary systems for lithium borosilicate glasses. Again it is found that the $K=1$ F data are closer to those for borate glasses than those for silicate glasses, as is made apparent by the simple binary average shown in the figure. We believe this is because the alkali is preferentially associated with the borate part of the network, as discussed above, and also because as $K$ increases, the Dell model\(^{(16)}\) tells us that there is a larger fraction of four-coordinated borons, $N_4$, in the borosilicates compared with the binary lithium borate glasses. The increase in $N_4$ causes the PF to be closer to that for borates than a simple average would dictate.

Figure 4 shows the packing trends of K, Rb and Cs borosilicate glasses. We observe that they do not exhibit peaks as for Li borosilicates. The packing fraction of K, Rb and Cs borosilicate glasses rise towards 0·64, which is the packing fraction for a dense random packing of equally sized hard spheres. At 0·64, these packing curves appear to level off. The K, Rb and Cs ions are much larger than oxygen, and because of this the boron coordination change from three-fold to four-fold does not appear to have an effect on the packing fraction trend.

(B) Alkaline earth borosilicate glasses

The calcium and barium borosilicate glass packing fraction curves lie in between the ionic (e.g. Cs) and covalent (e.g. Li) packing curves of the alkali borosilicate glasses as shown in Figure 5. Hence, we do not see a distinct covalent or ionic trend in these systems. Since the Ca and Ba ions are as large or
larger than the oxygen, we might expect to see the ionic trend in the PFs in these glasses, but due to their bivalency, oxygen is comparatively more abundant than in the alkali borosilicate glass systems. This oxygen abundance suppresses the dominant effect of the larger metal ions on the PFs (Figures 6 and 7). As with the alkali system, the PFs in barium and calcium borosilicate glasses rise towards the PF of the respective oxides as $X$ approaches 1.

Figure 8 and Figure 9 show a detailed plot of the PF data for the $K=1$ and binary systems for barium and calcium, respectively. The data for barium follow a trend similar to those for lithium and sodium, while calcium follows a different trend. We note that up to about $X=0.3$ the $K=1$ barium borosilicate PF data are much closer to the binary borate data than they are to the binary silicate data. For larger values of $X$, the $K=1$ barium borosilicate PF data become increasingly close to the average of the borate and silicate data (Figure 8). Contrastingly the $K=1$ calcium borosilicate PF data are close to the average of the borate and silicate data for all values of $X$ (Figure 9). There is no observed range in $X$ for which the $K=1$ calcium borosilicate PF data lie close to the binary borate data.
Conclusions

The packing fractions (PFs) of alkali and alkaline earth borosilicate glasses were studied and three distinct trends were observed. Packing in alkali borosilicate glasses having modifying ions smaller than oxygen (Li and Na) is dominated by the structural changes in the borate parts of the network. The PFs for lithium and sodium borosilicate ternary glasses are much closer to the PF for the respective borate binary glass than they are to the PF for the silicate binary glass (see Figure 3). For alkali borosilicate glasses having ions larger than oxygen (K, Rb and Cs), the packing is dominated by the modifying ions and the borate structural change does not have an apparent effect on the PF. Packing in alkaline earth borosilicate glasses is intermediate between the ionic and covalent packing trends observed for the alkali systems. This happens even though the modifying ions are as large as, or larger than oxygen, because there are half as many modifying ions added per oxygen in alkaline earth borosilicate glasses compared to alkali borosilicate glasses (MO versus M$_2$O).

Acknowledgements

This work was performed with the assistance of the National Science Foundation under grant DMR 0502051. Coe College is thanked for providing housing and stipends to the students.

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