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Comparisons of atomic arrangements in binary borate glasses with total, oxygen and modifier packing fractions

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Packing fractions provide a critical way of looking at glass density. By calculating how efficiently atoms fill space in the glass, we can deduce what structures are consistent with the packing. While our previous studies only used packing calculations that include all the atoms in the glass, our present study isolates the packing of oxygen and the packing of the glass modifier, expanding our data to depict the behaviour of these individual glass elements. Looking at modifiers Li, Zn, Mg, Ca, Na, Sr, Ba, Pb, Rb, Cs and K, our findings show the oxygen packing of the covalently packed glasses incorporating modifiers of Li, Zn, Mg, and Ca, generally follow similar trends to those of the four-coordinated borons in lithium borates, while ionically packed glasses, modifiers of Rb, Cs, and K, had packing closely related to the maximum random packing for a collection of two dissimilar spheres. Medium-sized modifiers acted as intermediates. We also found, for the ionic systems, the modifier can take up 3/4 of the volume of atoms. This affirms that for small modifiers, the oxygen network is relatively unaffected, but for large modifiers, the oxygen placement is dictated by the arrangement of the geometrically dominating atoms. We also lay out an argument for the use of crystal over ionic radii for these packing studies, and introduce an experimentally expanded zinc borate range of J=0·25–5·67; x=20–85 mol% zinc oxide used in the packing calculations, where J is the molar ratio of zinc oxide to boron oxide.

1. Introduction

1.1. Packing fractions

Oxide glasses, borates specifically, contain well-defined short range order atomic structures. These atomic arrangements alter the density of the glass. Packing fractions offer a perceptive unit-less density, showing how efficiently the atoms fill space.(1–4) Previous work with packing fractions uncovered two types of packing: covalent and ionic.(4,5) Covalent packing refers to packing in borates whose modifier has a radius at or less than oxygen and displays low packing efficiency due to the strong network forming ability of covalent oxygen. Ionic packing addresses the borates where the modifier's radius is much larger than oxygen and lends itself to high packing values similar to the random packing of spheres. It was suspected that covalently packed glasses have a principal structure governed by oxygen's covalently bonded network, while ionically packed glass principal structure is determined by the ionic bonding between the large modifiers and oxygen.(4,5)

While packing fractions provided a mathematical model, efforts were directed to correlating experimental nuclear magnetic resonance (NMR) data in borate glasses to the packing trends to determine if structure could be related to the packing calculations. The fraction of four-coordinated borons (N_4) has been seen experimentally to be a very prominent structural feature in borate glasses,(6–8) and those data were previously used to determine if the trends of total packing and structure aligned.(5) Random close packing for a collection of two dissimilar spheres is a calculation that depends on the composition and relative size of the atoms in question.(9) The results of this calculation allow for a comparison of packing behaviour to determine if the packing of a glass is similar to that of a random close packed structure of the same atoms.

Bista *et al*'s(4) approach using just total packing within the glass has limitations. The total packing provided a similarity to the trend of the four-coordinated borons but was not the best detailed analysis. Some glass systems matched the trend of random close packing, but it was unclear why. What was needed was a way to isolate the two factors embedded in the packing fractions. That is, we needed to separate the oxygen and the modifier from each other; while boron was ignored due to its extremely small volume. This would allow for determining which component

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dominated the packing, and therefore determined the structure of the glass. With minor manipulation of the packing calculation, we calculated the oxygen and the modifier packing fractions for the Li, Mg, Zn, Ca, Na, Sr, Ba, Pb, Rb, Cs, and K borate glasses ($MO/M_2O.B_2O_3$), providing intriguing clarification on glass structural behaviour based on geometry.

1.2. Zinc borates

The data used for zinc borate glasses come from a recently expanded modifier range produced by our research group. For the past several decades, the glass forming range of zinc borates was difficult to define in literature; the most common range for JZnO.B_2O_3 lies between $1\leq J\leq 2{\cdot}13$ (50–68 mol% modifier).(10) This range was limited by a relatively slow-cool/melt quench technique which allowed for phase separation in glasses $J<1$, and formation of a polycrystalline solid when $J>2{\cdot}13$.(10) If, however, we cooled the material quicker, a wider range of glasses could be made. Using plate quenching, which cools at a rate of 10 000°C/s, and roller quenching, at 100 000°C/s.(11) greatly shrinks the window for polycrystalline formation and phase separation, expanding the range of single phase zinc borate glasses.

2. Methods

2.1. Zinc borates

2.1.1. Sample preparation

Glass samples were made using 99% purity zinc oxide powder and 99% purity boric acid from Sigma-Aldrich. Using Equation (1)

$$J\text{ZnO}+2\text{H}_3\text{BO}_3\rightarrow J\text{ZnO}+\text{B}_2\text{O}_3+\text{H}_2\text{O} \qquad (1)$$

and the atomic masses of all elements, the gram amounts of ZnO and H_3BO_3 needed were calculated for 6 g batches. The batch, in a platinum crucible, was stirred thoroughly for 5 min and reweighed. The sample was placed in an electric Carbolite furnace at 1200°C for 15 min, removed and cooled to room temperature for a post-heat weight measurement. This weight was subtracted from the premelt, post-mix weight to determine the actual weight of the loss product, gaseous H_2O, and compared to the predicted weight loss (Figure 1). The differences are small. The glass as heated for an additional 10 min and quenched rapidly as described next to form glass.

Samples made in the established glass forming range were quenched between two steel plates, acetone washed before each use. This plate quenching produces large, clear, and durable samples of glass. Samples outside of the established glass range needed a faster cooling method to produce single phase samples. These samples were roller quenched; poured between two high speed spinning steel cylinders, which eject brittle glass a few microns thick into a collection bin.(11) The roller quenched samples sometimes contained isolated small streaks of crystal or phase separated glass. This was visually and readily removed.

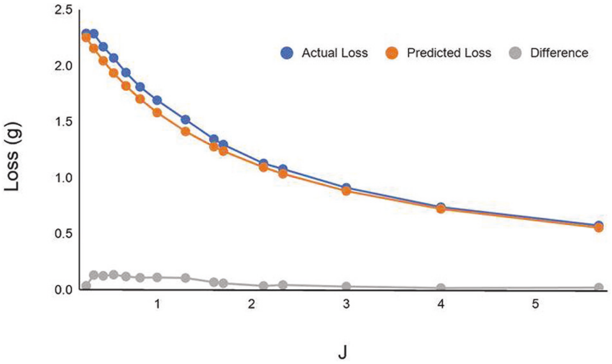

Figure 1. The trends of weight losses from the zinc borates. Shown are actual losses, predicted losses, and differences. The data points are larger than the error bars. J is the molar ratio of zinc oxide to boron oxide

2.1.2. Measurement of density and determination of the molar volume

A glass sample, typically greater than 0·5 cm^3, was weighed and added into a Quantachrome Ultrapycnometer 1000 that employed helium. The pycnometer ran once to determine the sample's volume, and the sample was placed aside for later use. To check the calibration of the instrument, small aluminium pellets with a measured volume of 0·1 cm^3 per pellet, were matched with the glass sample volume and placed in the pycnometer. The pycnometer ran the aluminium 15 times, with the last five runs used to determine the average pellet volume. After massing the aluminium the resulting density was found. This process was repeated with the glass sample and again with the pellets to ensure the continued accuracy of the pycnometer. The known density of aluminium,

*Table 1. Crystal and ionic radii (Å) from Shannon radii and coordination number of modifiers used in the packing calculations.(1) *Coordination number from the Materials Project(13) (zinc, lead and magnesium), $^{\partial}$Bista et al radii from Shannon Radii(4,14)*

		Radii (Å)	
Name	*Coordination*	*Crystal*	*Ionic*
Cs	10^{∂}	1·95	1·81
Rb	9^{∂}	1·77	1·63
K	8^{∂}	1·65	1·51
Ba	9^{∂}	1·61	1·47
Sr	8^{∂}	1·40	1·26
Ca	7-8^{∂}	1·23	1·09
O	2^{∂}	1·21	1·35
Na	6^{∂}	1·16	1·02
Pb	4*	1·12	0·98
Mg	6*	0·86	0·72
Zn	4*	0·74	0·6
Li	4^{∂}	0·73	0·59
B	3^{∂}	0·15	0·01

Table 2. Physical properties of zinc borate across the glass-forming range. The density for J=0 or pure B_2O_3 glass was taken from previous work from this group.[18] *The error in the density is 1%. J is the molar ratio of zinc oxide to boron oxide*

Glass composition (J)	*Atomic weight (amu)*	*Density (g/cc)*	*Molar Volume (cc/mol)*	*Total packing fraction*	*Oxygen packing fraction*	*Modifier packing fraction*
0·00	69·62	1·81	38·46	0·349	0·349	0·000
0·25	89·97	2·62	27·42	0·431	0·424	0·007
0·33	96·48	2·77	26·15	0·437	0·428	0·010
0·43	104·61	2·95	24·79	0·445	0·432	0·012
0·54	133·57	3·01	24·51	0·434	0·419	0·015
0·67	124·14	3·14	23·70	0·432	0·414	0·017
0·82	136·35	3·24	23·13	0·425	0·406	0·020
1·00	151·00	3·35	22·56	0·419	0·396	0·023
1·30	175·41	3·54	21·57	0·414	0·387	0·027
1·60	199·83	3·68	20·87	0·409	0·379	0·030
1·70	207·97	3·73	20·63	0·408	0·377	0·031
2·13	242·55	3·94	19·65	0·408	0·373	0·035
2·33	259·23	3·97	19·60	0·401	0·365	0·036
3·00	313·76	4·26	18·40	0·406	0·364	0·042
4·00	395·14	4·32	18·31	0·386	0·342	0·045
5·67	531·04	4·34	18·36	0·364	0·316	0·047

2·698 g/cm^3,(12) was used to correct the pellet density averages, and thus, the glass density average. This corrected value was recorded as the sample's density and is accurate to 1%.

Knowing the density, Equation (2) was used to determine the molar volume:(10)

$$V = \frac{J\left(m_{ZnO}\right) + m_{B_2O_3}}{\rho\left(J+1\right)} \qquad (2)$$

Where J is the molar ratio of modifying oxide to borate, m_{ZnO} and $m_{B_2O_3}$ the respective molar masses of zinc oxide and borate, and ρ is the density of the sample. Also, Equation (2) was used to calculate all molar volumes and the subsequent packing fractions by using the appropriate molar mass of each of the modifying oxides as well as the density of the respective glasses.

2.2. Ionic radii

Accurate radii are integral to determining atomic packing. Because the radii of atoms vary with coordination number, coordination for zinc, lead, and magnesium was determined through the crystal structure of the modifier (form MO where M is Zn, Pb, or Mg) through the database provided through the Materials Project.(13) Once the average coordination number of the ions was found, it was left constant at all compositions. Changes of the coordination number typically changes the radius by hundredths of an angstrom. When cubed, this propagates an absolute error of up to 10% but a relative error much smaller than that. However, trend comparisons remain useful. The coordination number was then used to determine which Shannon radii to use.(14) All values used for coordination and radii are displayed in Table 1. Included in Table 1 are coordination numbers and Shannon radii for Li, Na, K, Rb, Cs, Ca, Sr, Ba, and O taken from Bista *et al*.(4) The radius, and hence the volume of boron, was deemed negligible due to their very small relative size; for example, the volume of a boron ion is several hundred times smaller than oxygen. Therefore, boron was not included in any of the calculations.

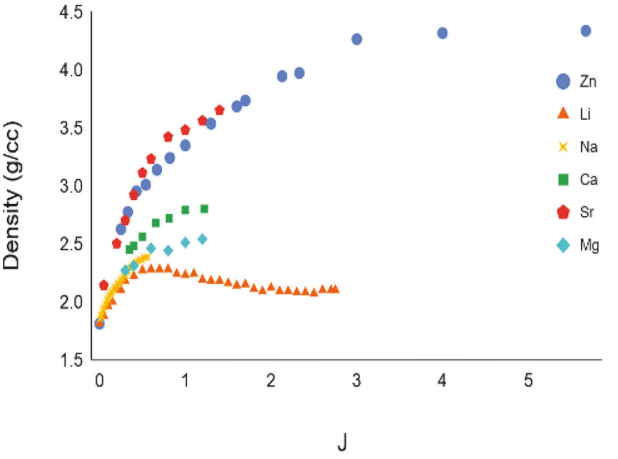

Figure 2. Collected densities of alkali/alkaline-earth borates and zinc borates.(15,18) *J is the molar ratio of modifying oxide to boron oxide. As expected, the more massive zinc ions cause zinc borates to be much denser since the volumes are similar. Data points are larger than the errors*

2.3. Calculating packing fractions

Density for the non-zinc binary borate glasses was gathered from Sciglass and our earlier published work(15–18) to calculate the molar volume using molar mass/density. Packing fractions (PF) were then calculated for all glasses using Equation (3)(4)

$$PF = \frac{\frac{4}{3}\pi\Sigma r_i^3 N_i}{V_m} \qquad (3)$$

where the summation adds each element, i, involved in a single composition, and r_i is the radius of the atom, N_i is the number of those atoms in a mole of

Table 3. Physical properties of lithium borate across the glass forming range. All density data were taken from previous work from this group.[18] *J is the molar ratio of lithium oxide to boron oxide*

Glass composition (J)	*Atomic weight (amu)*	*Density (g/cc)*	*Molar Volume (cc/mol)*	*Total packing fraction*	*Oxygen packing fraction*	*Modifier packing fraction*
0·00	69·62	1·81	38·5	0·349	0·349	0·000
0·05	71·11	1·88	36·0	0·363	0·360	0·003
0·10	72·61	1·96	33·7	0·379	0·374	0·005
0·15	74·10	2·00	32·2	0·388	0·380	0·008
0·20	75·60	2·11	29·9	0·410	0·399	0·011
0·25	77·09	2·10	29·4	0·409	0·396	0·013
0·30	78·58	2·18	27·7	0·425	0·409	0·016
0·40	81·57	2·22	26·3	0·435	0·414	0·021
0·50	84·56	2·27	24·8	0·446	0·420	0·026
0·60	87·55	2·28	24·0	0·450	0·419	0·031
0·70	90·54	2·28	23·4	0·451	0·416	0·035
0·80	93·52	2·28	22·8	0·452	0·414	0·038
0·90	96·51	2·24	22·7	0·445	0·404	0·041
1·00	99·50	2·23	22·3	0·445	0·401	0·044
1·10	102·49	2·24	21·8	0·448	0·400	0·047
1·20	105·48	2·19	21·9	0·439	0·390	0·049
1·30	108·46	2·18	21·6	0·437	0·386	0·051
1·40	111·45	2·18	21·3	0·438	0·385	0·054
1·50	114·44	2·16	21·2	0·435	0·380	0·056
1·60	117·43	2·14	21·1	0·432	0·375	0·057
1·70	120·42	2·15	20·7	0·435	0·375	0·060
1·80	123·40	2·11	20·9	0·427	0·367	0·060
1·90	126·39	2·09	20·9	0·424	0·362	0·062
2·00	129·38	2·12	20·3	0·430	0·366	0·064
2·10	132·37	2·09	20·4	0·425	0·360	0·065
2·20	135·36	2·09	20·2	0·425	0·359	0·067
2·30	138·34	2·08	20·2	0·424	0·356	0·068
2·40	141·33	2·08	20·0	0·424	0·355	0·069
2·50	144·32	2·07	19·9	0·423	0·353	0·070
2·60	147·31	2·10	19·5	0·429	0·357	0·073
2·70	150·30	2·10	19·3	0·430	0·356	0·074
2·75	151·79	2·10	19·3	0·430	0·355	0·075

the glass, and V_m is the molar volume. Equation (3) also calculates oxygen and modifier packing when just the oxygens or modifiers are summed.

2.3.1. Random packing of spheres

Maximum random close packing of binary spheres, (the two different spheres being the modifier and oxygen, as boron is ignored) can be calculated from the mass fraction (the total volume taken up by a particular species), and the radii of each sphere using Equations (4a) and (4b), where η_{rcp}=0·602 is the limit for random close packing of a single size of sphere (as reported in Santiso & Muller), and w_1 is the 'mass fraction' between the two spheres, or the fraction of the volume that is taken up by the larger species.[9]

$$\eta = \frac{\eta_{rcp}}{1-w_1\left(1-\eta_{rcp}\right)} \text{ for } w_1 < \frac{1}{2-\eta_{rcp}} \qquad (4a)$$

$$\eta = \frac{\eta_{rcp}}{w_1} \text{ for } w_1 > \frac{1}{2-\eta_{rcp}} \qquad (4b)$$

Because of the piecewise nature of these equations as well as the fact that in the definitional equations for packing the radii are cubed, precise values for the radii, and thus the coordination numbers are necessary. While packing fraction shows the relative amount of space filled by the atoms, the percent possible space-filling shows how much space the atoms take up when compared to how much space-filling is possible in a random close packed structure (η), given the size of the atoms. A fraction of the possible space-filling (η) can then be calculated by dividing the experimental packing fraction by the maximum random close packing fraction for dissimilar binary spheres.

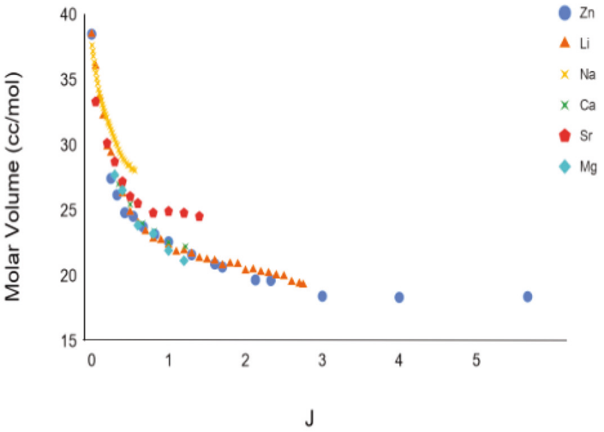

Figure 3. Comparison of zinc borate and collected alkali/alkaline-earth molar volumes.[15,18] *Data points are larger than the errors. J is the molar ratio of modifying oxide to boron oxide.*

3. Results and discussion

3.1. Zinc borates

By comparing our zinc borate density and molar volumes given in Table 2 to the alkali/alkaline-earth systems of lithium, sodium, calcium, strontium, and magnesium, we see a similarity of trends. Figure 2, a comparison of zinc borate and lithium borate density[(18)] (Table 3), shows the zinc borate to have higher density, despite a very similar molar volume, due to the high mass of the zinc ions. The trend for zinc borate density follows the trends of the other alkali and alkali-earth borates, see Figure 2. Calculated molar volumes of lithium borate glasses are compared to zinc borates in Figure 3, and to the other alkali and alkali-earth borates in Figure 3.[(15)] While the zinc borates are clearly much denser than lithium borate glasses, as evidenced in Figure 2, their molar volumes align in a downward curve, and behave much like the other glass systems, see Figure 3. These established trends support the idea that ZnO is similar in structure to Li_2O and other alkali and alkaline-earth oxides when in borate glasses.

3.2. Justification of crystal radii

In addition to coordination, the Shannon radii differ if measured in crystal or ionic form (Table 1). To determine which measurement made the most physical sense for our study, we compared the packing fractions of both radii, and compiled three arguments for the use of crystal radii over ionic.

3.2.1. The geometric argument for borates

Glassy boron oxide is arranged with one boron surrounded by three oxygen atoms. With the boron so small, we assume the oxygens touch to form an equilateral triangle. The centre to corner distance is equal to the boron to oxygen (B–O) bond length of 1·36 Å.[(14)] We then use a right triangle where the hypotenuse is the B–O bond length and the adjacent side is the radius of oxygen with a 30° angle in between. Using the properties of cosines we solve for the radius of oxygen and found it needs to be 1·18 Å to fit this triangle. This is closest to the crystal radius of oxygen of 1·21 Å.[(14)] The ionic radius of 1·35 Å for O from Shannon[(14)] produces an edge length of 2·70 Å, a length that is far off from the known value of 2·40 Å.[(19)] Note that this argument does not apply to other glass systems such as silicates or germanates.

3.2.2. The boron oxide packing argument

After calculating packing fractions using both crystal and ionic radii, see Figure 4, we found *J*=0, or pure boron oxide glass, to be quite different for the crystal and ionic radii packing fractions. This can help decide which packing fraction is the most accurate.

We would expect the ratio of the packing fractions of crystalline and glassy B_2O_3 to be equal to the ratio of the crystal and glassy densities, since this represents an efficiency of packing of the same number and kinds of atoms. For glassy B_2O_3 to achieve a density of 1·81 g/cm^3,[(18)] we expect a packing fraction of the glass to be 0·362. This is calculated by employing a density of 2·46 g/cm^3 and deriving a packing fraction of 0·492 for the crystal from a cell volume, found from x-ray analysis, of 135·9 Å^3 and the number, kinds, and masses of atoms in the unit cell of crystalline B_2O_3.[(20,21)] This methodology supports the use of crystal radii for amorphous packing fractions as the packing fraction calculated using crystal radii, 0·349, is significantly closer to the expected packing fraction of 0·362 than that calculated using ionic radii, 0·484.[(14)] Note that this assumption might break down if the radii are allowed to change between crystalline and glassy states, but works sufficiently for our present case.

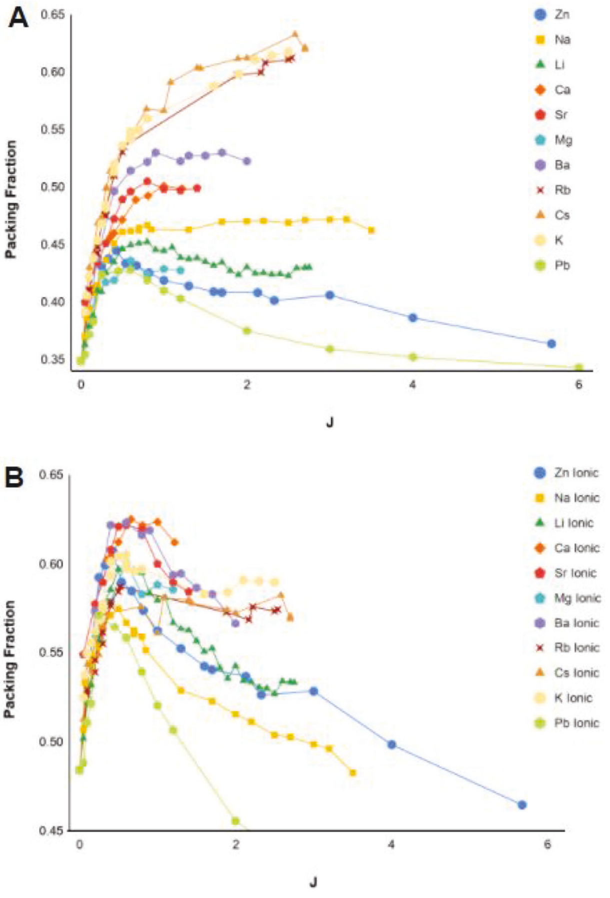

Figure 4. (a.) Packing fractions for alkali/alkaline-earth systems calculated with Shannon crystal radii compared to (b.) Packing fractions of the same systems calculated with Shannon ionic radii. At J=0, or pure borate glass, the packing varies dramatically, and the crystal radii create trends in predictable places, increasing packing with the radius of the modifier while the ionic packing displays a comparatively random assortment of packing trends. J is the molar ratio of modifying oxide to boron oxide.

3.2.3. The consistency argument

Ionic radii give inconsistencies in packing trends. As seen in Figure 4, a comparison of the order of appearance from highest to lowest packing, the crystal radii cluster like sizes with like packing. The largest modifiers, Rb, K, Cs, have the highest packing fractions, the smallest modifiers, Li, Zn, Mg, have the lowest packing fractions, with the medium sized modifiers, Na, Sr, Ca, Ba, lying between the two in a consistent manner (Pb doesn't follow this due to its dual role as a glass former and a glass modifier, this will change its packing in other ways). This gives a link to size and packing. The ionic radii give no such explainable order. The large modifier potassium is between medium sized modifier strontium and smaller lithium, separated from the like Rb and Cs by the smallest modifiers, Zn and Mg. This lack of consistency calls the ionic radii into question and further supports the use of crystal radii for research.

As a result of these arguments, we chose to employ Shannon's crystal radii over the ionic radii.(14)

3.3. Packing fractions

To examine the correlations of structure to packing in lithium borate glasses we needed to compare the known fraction of four-coordinated borons (N_4)(8) to their packing fractions. (Figure 5). However, comparison to just the oxygen packing rather than total packing produced a much better correlation (Figure 5). We compared these N_4 data to the oxygen packing of other borate systems whose modifiers are similar in size to lithium in that the packing is controlled by oxygen, which is by far the largest ion for these cases: zinc, lithium, magnesium, and calcium (Figure 6). This is based on the assumption that the glasses have comparable structures and employs the fact that the N_4 values are most well known in the lithium borate

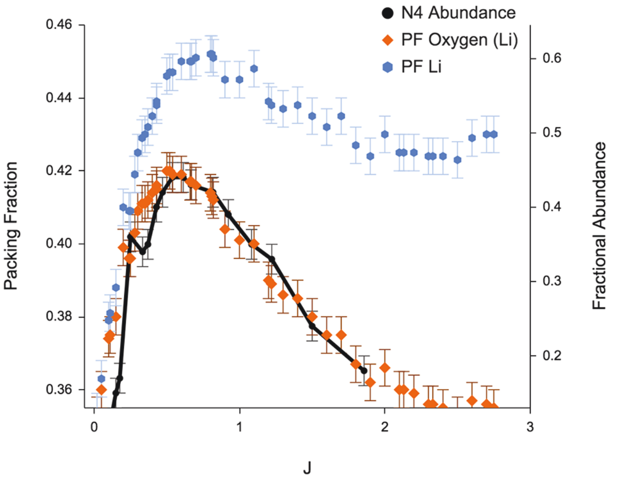

Figure 5. Comparing the N_4 trend to total packing of lithium borates (blue) and oxygen packing (orange) in the same lithium borate glasses. The N_4's fit to the oxygen packing is notably superior to the total packing. J is the molar ratio of lithium oxide to boron oxide. Although the total packing levels out at high J, the oxygen packing continues to decline with the trend of N_4

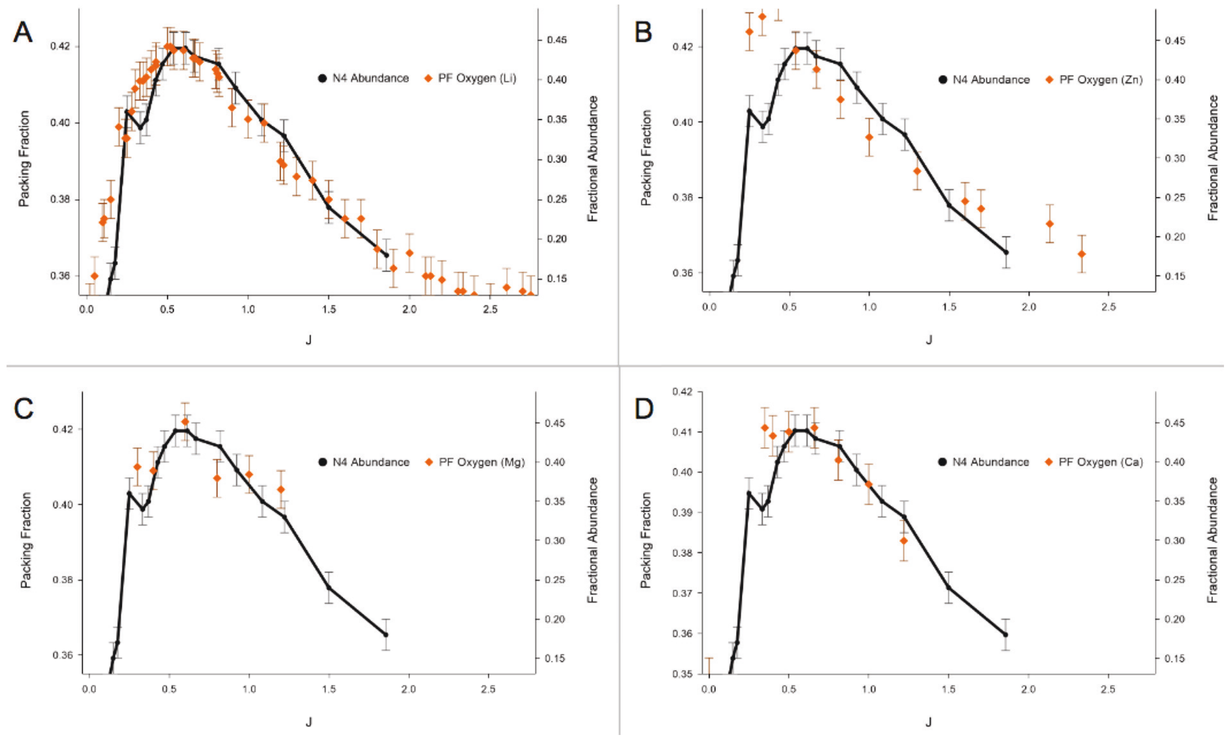

Figure 6. The fraction of four coordinated borons(8) in lithium trends fitted to the oxygen packing of (a) lithium, (b) zinc, (c) magnesium, and (d) calcium borate glasses. A strong correlation is observed in all cases. J is the molar ratio of modifying oxide to boron oxide

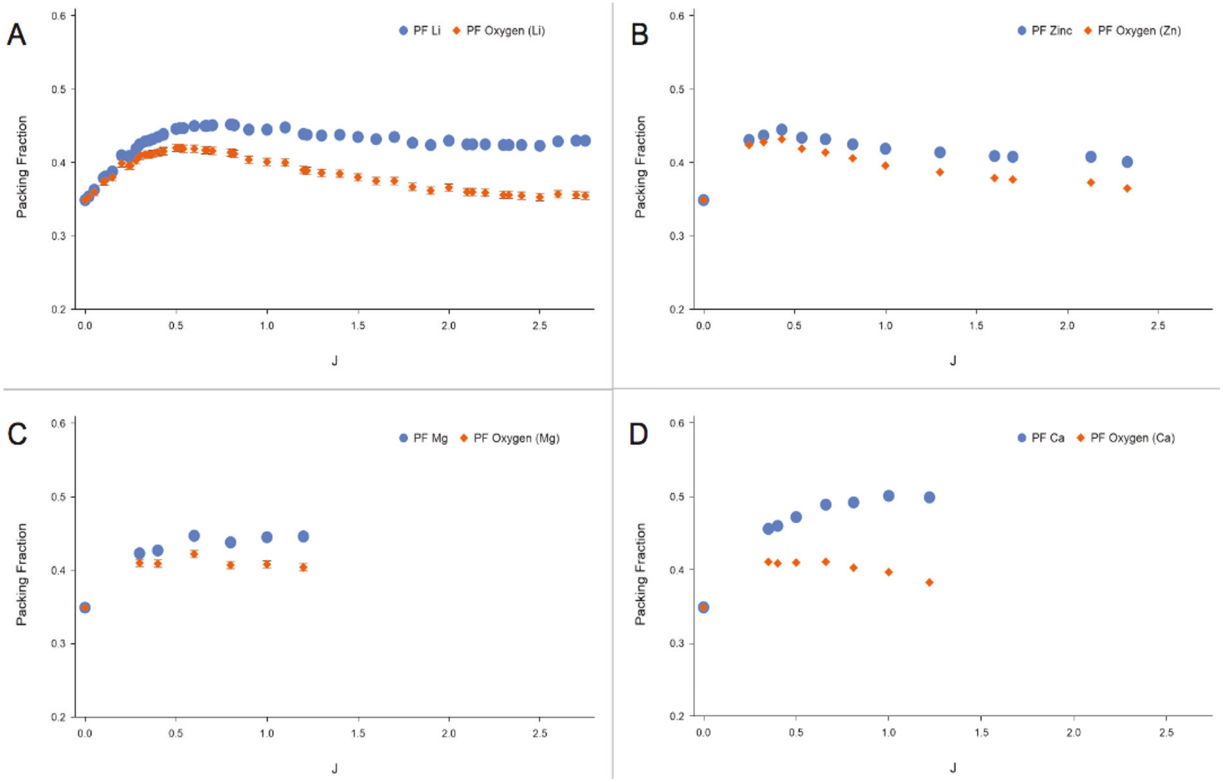

Figure 7. Total packing fraction and oxygen packing fraction of (a) lithium, (b) zinc, (c) magnesium, and (d) calcium borate glasses. A close correlation between the total and oxygen packing is observed. Data points are comparable to or larger than error bars. J is the molar ratio of modifying oxide to boron oxide

system for these four small modifiers but are known to be generally close in trend but lower in values compared to lithium borates.$^{(22,23)}$ This oxygen packing correlation to the N_4 trend similarity suggests not only that the N_4 is a controlling short-range structure of the boron–oxygen linkages, but that this structure can be identified through the oxygen packing trend (Figure 6). What is of particular interest is the similarity of the oxygen packing and the total packing trends of these covalently packed glasses (Figure 7). This suggests the relative amounts of three- and four-coordinated boron units dominate the total packing of these glasses. However, this total and oxygen packing correspondence does not hold for other systems. The oxygen packing for all systems in Figure 8 display three distinct groupings corresponding to radii, with

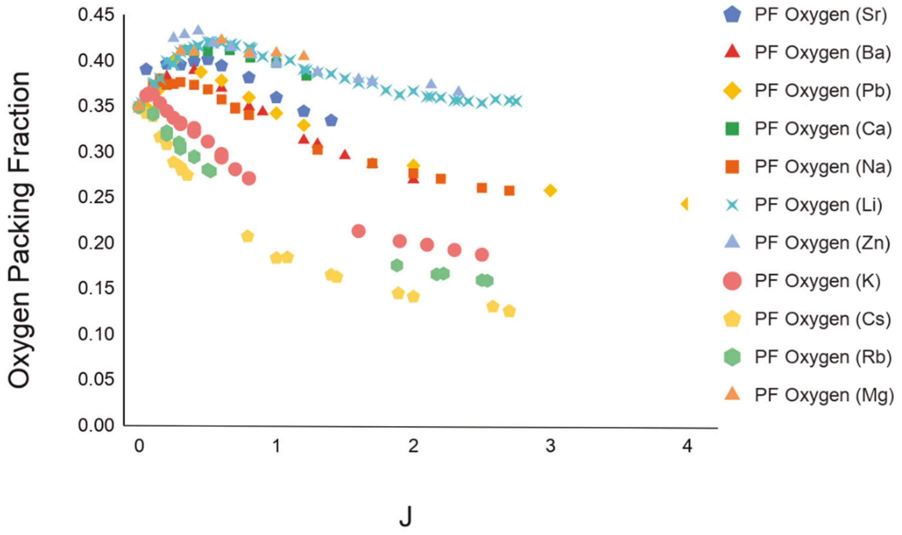

Figure 8. Oxygen packing of all glasses studied. Three groupings are seen corresponding to radii, with the covalent glasses of Li, Zn, Mg, and Ca borates at the highest packing, the ionic glasses of Rb, Ca, and K borates with the lowest, and Na, Sr, Pb, and Ba borates acting as intermediates. J is the molar ratio of modifying oxide to boron oxide.

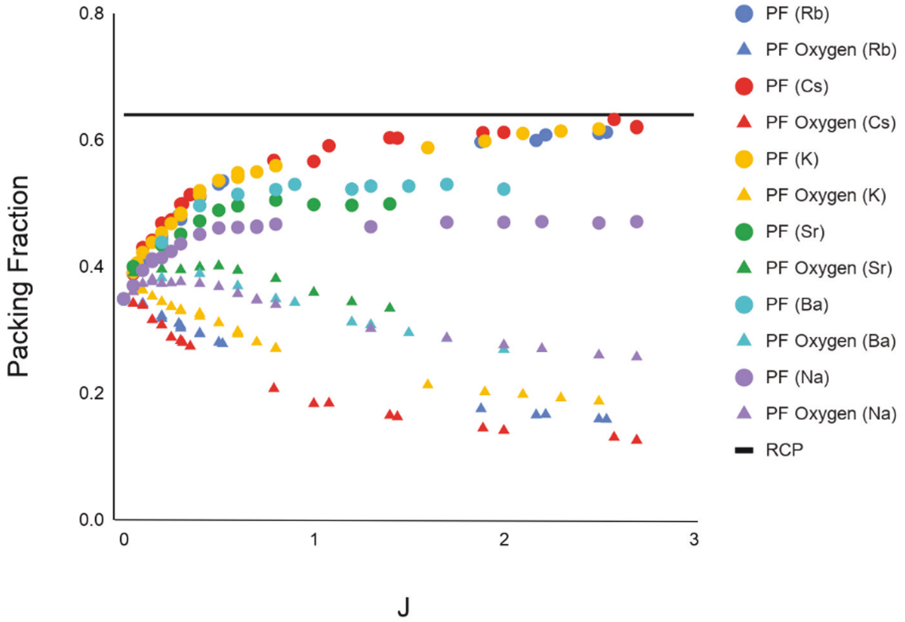

Figure 9. Packing fraction and oxygen packing of binary borate glasses whose modifier is larger than oxygen. The oxygen packing across all systems depletes as the packing rises up to the maximum random packing of single-sized spheres (RCP); 0·64, see horizontal line in graph.(24) *Data points are larger than error bars. J is the molar ratio of modifying oxide to boron oxide*

the covalent glasses of Li, Zn, Mg, and Ca borates at the highest packing, the ionic glasses of Rb, Cs, and K borates with the lowest, and Na, Sr, Pb, and Ba borates acting as intermediates.

The most notable difference in the large modifier systems is the dramatic decrease in packing efficiency of the oxygens, no longer holding any resemblance to the fraction of four-coordinated borons. Yet, as the amount of modifier increases, the total packing of the glass approaches the maximum random packing of single-sized spheres, 0·63(24) for K, Rb, and Cs borate glasses, see Figure 9. This is sensible since these modifiers are much larger in volume than oxygen and approximate single sphere random close packing. For the intermediate cases of Na, Sr, and Ba, the packing also levels out, but below 0·63, see Figure 9. For the individual case of Pb, the total packing is initially covalent and increases with the N_4 in lead, but falls more rapidly than N_4 at higher *J*, as seen in Figure 10.(25) At large *J*, the packing levels out near 0·35, around the packing of pure borate glass. This implies these high *J* glasses (*J* near 6) may require a second network to form, primarily composed of lead oxide, to form such highly modified glasses and to maintain such a low packing fraction trend. Furthermore, the coordination of Pb likely changes quite a bit over this large range of glass compositions and the approximation that these atoms are spherical may break down for the lead case.(26,27)

To further assess the possibility of random packing, we calculated the maximum random packing for a collection of two dissimilar spheres, a calculation dependent on glass composition and the volume ratios of the atoms, i.e. the modifier and the oxygen with the boron negligible in comparison. Santiso & Muller's methods give the random packing of binary spheres.(9) They range from the random packing of single spheres, 0·60, up to about 0·84 for the potassium borate case (here we consider only potassium and oxygen and ignore boron). For the lithium case, the maximum packing is about 0·73. The other systems approach the potassium value. These higher packing values result from the smaller ions filling interstitial space formed by the larger ions.

We then compared the total packing to their respective random packing trends, by determining the ratio of how much of the space was filled to the space that could theoretically be filled with atoms

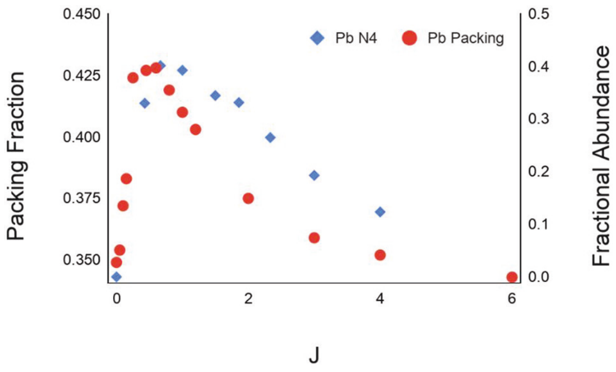

Figure 10. The total packing against the fraction of four-coordinated borons (N_4) of lead borate glasses.(25) *The packing rises with the N_4 but falls more rapidly as we increase the amount of lead past J=0·6. J is the molar ratio of lead oxide to boron oxide*

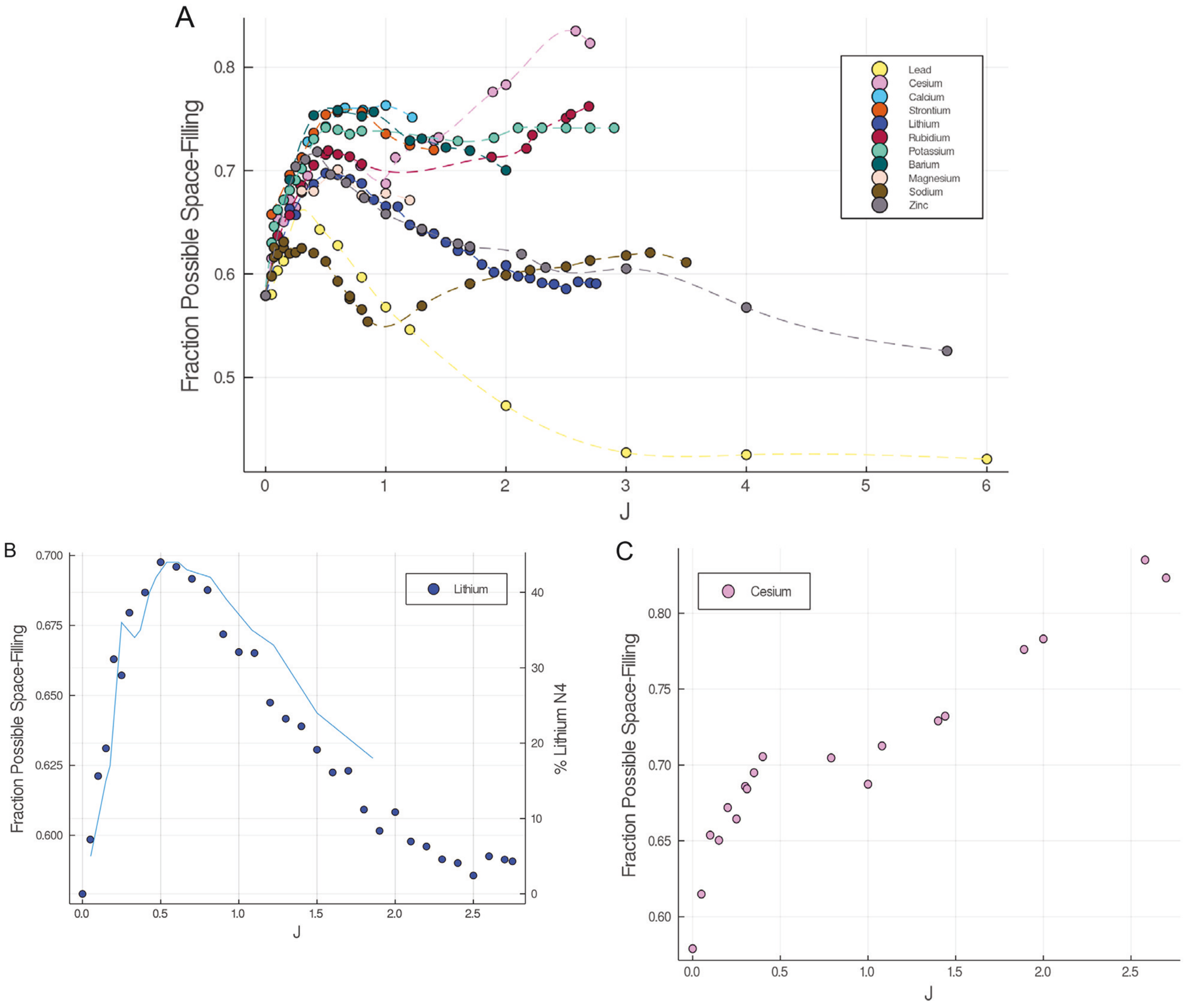

Figure 11. (a) Fraction of possible space-filling of all studied species as calculated from a model of random close packing of similar spheres.(9) Curves are smoothing splines and intended only as a guide for the eye. (b) A comparison of the lithium species is also made to the lithium borate NMR experimental N_4 fraction (blue line) in which the lithium space-filling follows closely to the NMR fraction of four coordinated borons. This trend similarity is not seen in (c) caesium which continuously increases past 80% of its possible space-filling via random packing. This further suggests the random assortment of atoms in caesium and other ionically packed glasses. J is the molar ratio of modifying oxide to boron oxide

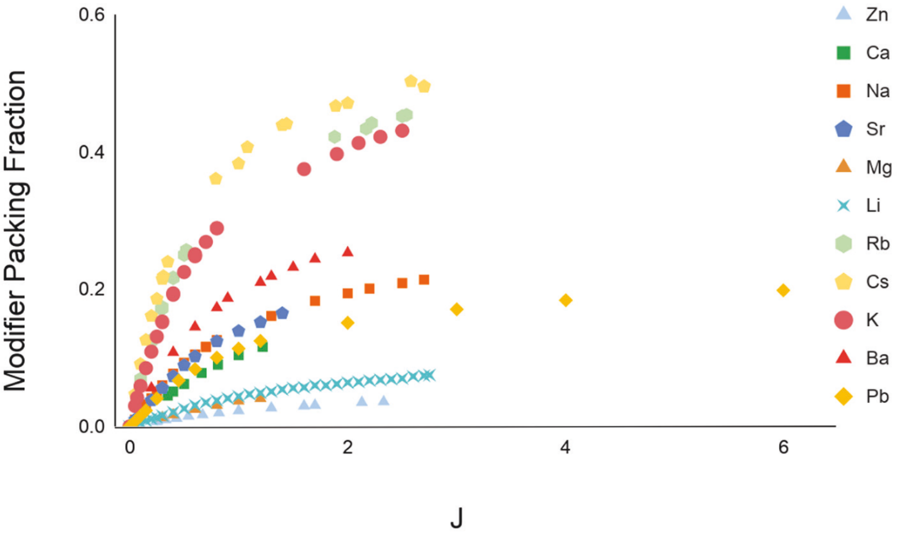

Figure 12. Modifier packing of zinc, calcium, magnesium, lithium, sodium, strontium, lead, barium, rubidium, caesium, and potassium borate glasses. Zinc, calcium, magnesium, and lithium take up little of the glass volume, while rubidium, caesium, and potassium make a considerable contribution to the volume of the glass. Data points are larger than error bars. J is the molar ratio of modifying oxide to boron oxide

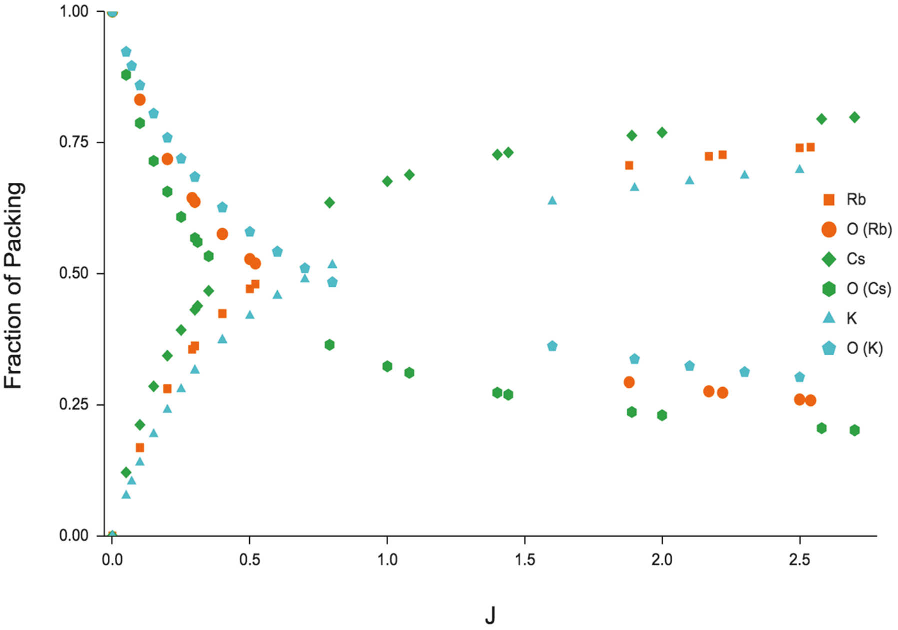

Figure 13. The fraction of the modifier packing to total packing, and oxygen packing to total packing for large modifiers. Of the volume of the glass taken up by atoms, this graph depicts the fraction of volume of modifier versus oxygen at a given J. At high J, the fraction of volume levels out at ¾ modifier and ¼ oxygen. J is the molar ratio of modifying oxide to boron oxide

(Figure 11(a)). The lithium system follows the trend for N_4, once again alluding to a relationship between N_4 units and the structure in the glass (Figure 11(b)). Covalently packed glasses mostly plot together in Figure 11(a), reaffirming their structural similarities to each other and thus to the presence of four-coordinated borons seen in lithium; with sodium deviating somewhat. In the larger modifier glasses, a similar trend from the percent possible space-filling to the model of the fraction of four-coordinated boron is not observed. This is seen, for example, in the trend of caesium borate glasses in Figure 11(c) in contrast to lithium in Figure 11(b), where caesium's packing efficiently increases continuously to 80% of its possible allotment. This is further evidence that the modifier is the dominant structural factor for ionically packed glasses, resulting in an atomic arrangement that is more disordered as more modifier is added.

Variation of modifier packing is seen in Figure 12. Typically, ions whose radii are at or below that of oxygen (Zn, Mg, Ca, Li, Pb) obtain a minimal amount of the available volume in modified borate glass, these occupy the lowest grouping of trends. This implies the borate network structure can support the increasing amount of modifier if the modifier is small enough to fit interstitially between the favoured oxygen structure. Modifier radii larger than oxygen rapidly increase their contribution to the overall glass volume and this trend plateaus as *J* increases, see Figure 12. When looking at the volume taken up only by atoms, the large modifiers (Rb, Cs, K) reach up to ¾ of the available volume (Figure 13). These modifiers dominate the volume in the glass and give insight into the diminution of the importance of oxygen packing in these large alkali glasses.

Conclusion

Our study revealed the total, oxygen, and modifier packing fractions for a variety of binary borate glass systems. The results showed three distinct groupings of glass systems. The covalently packed glass systems showed a dominance of oxygen in the packing, as well as evidence towards seeing four-coordinated boron structures through the oxygen packing. The ionically packed glasses showed a packing dominance of the modifier, with the total packing approaching the trends for maximum random packing for a collection of two dissimilar spheres. An intermediate grouping was found between the two extremes. We suggest the agent defining these distinct packing groups is the modifier radius size. An oxygen network controls packing when it can form around modifiers whose radius is less than or equal to that of oxygen but fails to control packing when the modifier's radius is larger than oxygen.

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