

DIFFERENTIAL VOLUME CHANGES IN TRIGONAL AND TETRAHEDRAL BORATE UNITS

Gregory J. Ongie*, Steven A. Feller, and Mario Affatigato
Physics Department, Coe College, Cedar Rapids, IA 52402, U.S.A.

Masao Kodama
*Department of Applied Chemistry, Sojo University, 4-22-1 Ikeda Kumamoto, 860-0082
Japan*

For the alkali borate systems, density trends may be used as an indicator for structural changes within a glass. However, with the use of high-precision density data, we may be able to indirectly observe superstructural changes in the glass by applying the differential volume technique used by Doweidar on various silicate and borate systems. This technique allows us to examine the differential changes of the volumes of the 3-coordinated trigonal units and the 4-coordinated tetrahedral units (named and fractionally given by the f_1 and f_2 units, respectively) as a function of R (up to $R < 0.6$, where R is the mole ratio of alkali oxide to boron oxide). The relative volumes of the borate units are not constant in the low R region, but contain features that may correspond to when a short-range unit is participating in large superstructural units. We also applied this same analysis to the barium borates, and found that the trends of the unit volumes are nearly identical to those for the sodium borates, perhaps indicative that the superstructural changes are also identical for both the alkali borate and alkaline-earth borate systems. Finally, a comparison of our results with Kroeker's recent ^{11}B MAS NMR studies reveal that features in the unit volumes may correlate to changes in the abundance of the two observed f_2 species.

Of recent interest in the study of alkali borates and related glass systems is the question of intermediate range structure. Currently, only a few methods have proven sensitive enough to detect the presence of such superstructural groups, such as NMR, neutron scattering, vibrational spectroscopy, and laser desorption time-of-flight mass spectroscopy^(1,2,3,4,5). However, using the analysis employed in this study, it is possible to extract information that may be related to superstructural changes from a set of density data, provided it is of sufficient accuracy and resolution.

The aforementioned technique was originally devised by Doweidar⁽⁶⁾ which itself was an extension of the density model proposed by Shibata *et al.*⁽⁷⁾ In Shibata's model, average values for the total volume of each of the structural units, including empty space and contributions from associated alkali, were calculated using a density data set and a model for the unit abundances. Doweidar, rather than calculating an average value for the volumes, calculated the volumes as a function of composition, which he was able to do because of the high precision of much of his density data.

The purpose of this study is to update and extend Doweidar's original work on the alkali borates using recent high precision density data, and to compare the results with recent NMR-based structural studies.

Procedure

Two sets of information are necessary for this analysis: high precision density data and the fractional abundances of the structural units as a function of composition. The density data used in this study were obtained from samples prepared for velocity of sound measurements using the solution method^(8,9,10,11,12,13). Each sample was cast and

annealed in a cylindrical mold 15 mm in diameter and 30 mm deep, and then chemically analyzed to determine its composition by means of the manninol method⁽¹⁴⁾.

Measurements of density were made using a hydrostatic weighing method with a silicon single crystal as the density standard⁽¹⁵⁾, resulting in an estimated uncertainty of ± 0.001 g/cc.

The model used for the fractional abundances of the structural units is alkali-independent and was presented by Chong *et al.*⁽¹⁶⁾, which is consistent with the results of many NMR studies^(17,18,4). The structural units relevant to this study are the f_1 unit, a trigonal BO_3 unit with all bridging oxygens, the f_2 unit, a tetrahedral BO_4 unit with all bridging oxygens and an associated alkali cation, and the f_3 unit, a trigonal BO_3 unit with one non-bridging oxygen and an associated alkali cation. In the alkali-independent model, the fractional abundance of the f_1 unit in the region $0.0 \leq R \leq 0.7$ is given by $f_1 = 1 - R$, where R is the mole ratio of alkali oxide to boron oxide. The fractional abundance of the f_2 unit in the region $0.0 \leq R \leq 0.4$ is given by $f_2 = R$, and for $0.4 \leq R \leq 0.7$, $f_2 = R/6 + 1/3$. Also, the fractional abundance of the f_3 unit in the region $0.4 \leq R \leq 0.7$ is given by $f_3 = 5R/6 - 1/3$. However, the data sets used in this study primarily span the compositional region $0.0 \leq R \leq 0.5$. Thus, the volumes of only the f_1 and f_2 units two units can be reliably analyzed in this study, as they are the only two present in sufficient quantity in this region.

To begin the calculation, we define the glass density in terms of its dimensionless mass relative to pure borate glass ($R=0$), $m'(R)$, and its dimensionless volume relative to pure borate glass, $v'(R)$:

$$\rho(R) = \frac{m(R)}{v(R)} = \frac{m'(R)}{v'(R)} \cdot \rho(0), \quad (1)$$

$$v'(R) = \frac{m'(R)}{\rho(R)} \cdot \rho(0), \quad 3$$

(2)

where $\rho(0)$ is the density of vitreous B_2O_3 . $m'(R)$ can simply be calculated by the ratio of the molecular weight of the glass at composition R to the molecular weight of the pure borate glass. Also, we can interpret $v'(R)$ as the sum of the fractional abundance of each unit multiplied by its volume relative to the f_1 unit (given by v_1 and v_2 , respectively):

$$v'(R_1) = f_1(R_1) \cdot v_1 + f_2(R_1) \cdot v_2 \quad (3a)$$

$$v'(R_2) = f_1(R_2) \cdot v_1 + f_2(R_2) \cdot v_2, \quad (3b)$$

where R_1 and R_2 are the R-values of two adjacent points in the density data set.

Replacing $v'(R_1)$ and $v'(R_2)$ with the expression derived in equation 2 gives:

$$f_1(R_1) \cdot v_1 + f_2(R_1) \cdot v_2 = \frac{m'(R_1)}{\rho(R_1)} \cdot \rho(0) \quad (4a)$$

$$f_1(R_2) \cdot v_1 + f_2(R_2) \cdot v_2 = \frac{m'(R_2)}{\rho(R_2)} \cdot \rho(0). \quad (4b)$$

All the variables except v_1 and v_2 in equations 4a and 4b are known: $f_1(R_1), f_2(R_1), f_1(R_2), f_2(R_2)$ are defined by the fractional abundances model ($f_1 = 1-R, f_2 = R$); $\rho(0), \rho(R_1)$, and $\rho(R_2)$ are obtained from our density data set; and $m'(R_1)$ and $m'(R_2)$ can be calculated from the respective molecular weights. Therefore, since R_1 and R_2 are close in value, we can make the approximation that the solutions for v_1 and v_2 are defined at the composition $(R_1+R_2)/2$.

Additionally, some of the density data sets range up to approximately $R = 0.6$. As noted earlier, in the region $0.4 \leq R \leq 0.7$, trigonal units with one non-bridging oxygen (f_3

units) begin to appear. However, we found that extending this analysis to regions where three structural units exist presents some difficulties. The main problem is that the R-values at which the unit volumes are defined would have to be obtained by averaging over three values, yielding results that would only be acceptable if the resolution of the density data was extraordinarily fine. However, a useful approximation is to hold one of the unit volumes constant (f_3), using the average volume derived from a least squares analysis over the entire data set, and proceed with the calculation letting the other two unit volumes vary (f_1 and f_2).

Also, we collected two sets of density data for the sodium borate system taken over the same composition range, one filling in the compositions between the other, resulting in data of twice the compositional resolution. To remove a very slight systematic error, we averaged adjacent points in the data set, yielding a set of the same resolution as the other alkali systems.

Finally, using the value of 1.838 g/cc for the density of vitreous B_2O_3 ⁽¹³⁾, the volume of the f_1 unit at $R = 0$ can be calculated to be 31.45 \AA^3 (referred to as V_0 in this paper), which can then be used to convert the relative volumes into absolute volumes.

Results and Discussion

For the volume of the f_1 units in the region $0.0 \leq R \leq 0.4$, we find that the trends initially reach one minimum and then one maximum, with the exception of the lithium system, which appears to be monotonically decreasing [Figure 1]. The minimum in the

trends is at $R = 0.18 \pm 0.05$, and the maximum is at $R = 0.30 \pm 0.05$, where there is also a slight alkali dependence in the magnitude of the minimum and maximum—greater for systems with larger alkali—and at most deviating approximately 10% from V_0 , the volume of the f_1 unit at $R = 0$. Nevertheless, the f_1 units for each system appear to have approximately the same average volume in this region of roughly $0.97 \cdot V_0$. This is consistent with the fact that the composition of the f_1 unit is alkali independent.

For the volume of the f_2 units in the region $0.0 \leq R \leq 0.4$, we find that trends initially reach a broad maximum and then a slight local minimum, again with the exception of lithium, which appears to be monotonically increasing [Figure 2]. Additionally, there is a small sharp feature at low R in the trends (with the exception of potassium), which reaches a maximum at $R = 0.05 \pm 0.01$ for the lithium and sodium systems, and at $R = 0.02 \pm 0.01$ for the rubidium and cesium systems. The broad maximum in the compositional trends is at $R = 0.18 \pm 0.10$, and the local minimum is at $R = 0.30 \pm 0.05$, mirroring the changes seen in the f_1 unit.

Unlike for the f_1 unit, there is a very clear alkali dependence on the volume of the f_2 unit. Such a dependency is explainable by the fact that alkali cations are only associated with f_2 units. To quantify this observation, we performed a least squares analysis to determine the best fit average value for v_2 over the entire range of available compositions. Plotting these values versus the volume of the alkali ion^(19,20) yields a linear relationship given by:

$$(Best\ Fit\ v_2\ in\ \text{\AA}^3) = 1.43 \cdot (Volume\ of\ alkali\ ion\ in\ \text{\AA}^3) + 26.8, \quad (5)$$

with an R^2 value of 0.997 [Figure 3].

In addition, we applied the differential volume technique to data we obtained from the barium borates. Spectroscopic data indicates the fractional abundance of the f_1 and f_2 units in barium borates appear to follow the same $f_1 = 1 - R$, $f_2 = R$ dependency as in the alkali borates in the low R region^(21,17). Using this fact, we were then able to calculate the volumes of its f_1 and f_2 units, and we proceeded to plot them with the results from the sodium borate system as a comparison [Figure 4]. Sodium was chosen because the ratio of the cubes of the ionic radii of Ba to Na is roughly 2:1⁽¹⁹⁾, yet in sodium borates there are twice as many ions per mole than in barium borates, thus we would expect the volumes of the units to be comparable if the systems are isostructural. Due to the similarity observed between the unit volume trends in the sodium borates and the barium borates, we believe that the superstructural changes hypothesized for the alkali borates may extend to the alkaline-earth borate systems, and could possibly be an intrinsic property of the borate network itself. Due to the phase separation in low R barium borates, we are limited in our comparison to the region $0.2 \leq R \leq 0.4$.

We also tried to extract information about the volume changes of the f_1 and f_2 unit in regions past $R = 0.4$ by holding the f_3 unit volume constant. Of the data sets available, we found that rubidium and cesium were the only two which extended far enough past $R = 0.4$ to warrant analysis. Thus, we performed a least squares analysis on these two data sets to find the best fit average value over the entire range of available compositions for the volume of the f_3 units. Comparing our values to those obtained by Lower *et al.*⁽²²⁾, we found that our values were within about 10% of theirs. However, Lower's data cover the

entire range of composition for which the f_3 unit is present ($0.4 \leq R \leq 2.1$), but our data are limited to only when the f_3 unit first appears ($0.4 \leq R \leq 0.6$). Since the difference between our values is small, though the difference between our ranges is large, we believe that holding the f_3 unit volume constant serves as a suitable approximation.

The above analysis reveals that the volumes of the f_1 unit in rubidium borates and cesium borates drop to another minimum at about $R = 0.53 \pm 0.05$ of about $0.85 \cdot V_0$, and the f_2 unit volume trends reach a maximum in the same area of about $2.4 \cdot V_0$ for cesium and $2.0 \cdot V_0$ for rubidium [Figure 5].

Comparing our results to those in the original study by Doweidar⁽⁶⁾, we find that his results are remarkably comparable to ours, albeit his are somewhat less accurate. For example, the maxima and minima in his unit volumes appear to be offset by roughly $+0.5 R$ from ours. Additionally, from our analysis we were able to observe fine peaks in the volume of the f_2 units at low R , but such features are absent from Doweidar's results.

Unlike when this analysis is performed on alkali silicates⁽²³⁾, we find that in the alkali borates the volume of the units varies extensively as a function of composition. We hypothesize that this is due to the presence of certain superstructural units in which the f_1 and f_2 units are participating, affecting the net volume of these short-range units.

Recent ^{11}B MAS NMR studies on cesium borates by Kroeker *et al.*⁽¹⁾ and Ratai *et al.*⁽⁴⁾ indicate the existence of two distinct species of f_2 units present in the $0.0 \leq R \leq 0.6$ region, separated by roughly 1 ppm in the ^{11}B MAS NMR spectra, which are believed to correspond to f_2 units participating in two different superstructural environments. Quantitative analysis of Kroeker's data reveals that from $0.0 \leq R \leq 0.2$, the two species of f_2 are present in roughly equal quantities, from $0.2 \leq R \leq 0.35$ the species characterized

by the lower chemical shift (the “lower frequency species”) is created preferentially over species characterized by the higher chemical shift (the “higher frequency species”) by approximately 3:2, from $0.35 \leq R \leq 0.45$ a crossover occurs in the trends, and from $0.45 \leq R \leq 0.6$ the higher frequency species is created preferentially over the lower frequency species by approximately 2:1.

The changes in abundances of the different f_2 species that occur from $0.2 \leq R \leq 0.35$ and $0.45 \leq R \leq 0.6$ appear to align with events in our analysis of the changes in the volumes. In the cesium system, we find that at approximately $R = 0.3$ the f_2 unit volume reaches a local minimum, and at approximately $R = 0.55$ reaches a local maximum. Such a correlation leads us to speculate that the lower frequency species may exhibit more efficient packing than the higher frequency species, resulting in the changes in net volume of the f_2 unit we observed in this study.

Conclusion

We performed an analysis of the differential volume changes of the f_1 and f_2 units of alkali borates glasses as a function of composition and found that the volumes of the units vary extensively over the composition $0.0 \leq R \leq 0.6$. The volume of the f_1 unit appears to be independent of alkali when compositionally averaged, while the f_2 unit average volume varies linearly with that of the associated alkali. The same analysis was then applied to barium borates which we found to exhibit trends similar to the alkali borates. Finally, we also compared our results to f_2 speciation observed in recent ^{11}B MAS NMR data, and we found that they contained compositional features which correlated to the minima and maxima of the unit volumes calculated in this study.

Acknowledgements

This work was supported by the National Science Foundation under grants DMR 0211718, DMR 0502051, NSFINT 0089510. Coe College is thanked for providing additional support.

References

- 1) Kroeker, S., Feller, S.A., Affatigato, M., O'Brien C.P., & Clarida, W. *Phys. Chem. Glasses*, 2003, **44** (2), 54-58.
- 2) Sinclair, R.N., Stone, C.E., Wright, A.E., Polyakova, I.G., Vedishcheva, N.M., Shakhmatkin, B.A., Feller, S.A., Johanson, B.C., Venhuizen, P., Williams, R.B., & Hannon, A.C. *Phys. Chem. Glasses*, 2000, **41** (5), 286-289.
- 3) Kamitsos, E.I. *Phys. Chem. Glasses*, 2003, **44** (2), 79-87.
- 4) Ratai, E.-M., Janssen, M., Epping, J.D., Chan, J.C.C., & Eckert, H. *Phys. Chem. Glasses*, 2003, **44** (2), 45-53.
- 5) Affatigato, M., Feller, S., Schue, A., Blair, S., Stentz, D., Smith, G., Liss, D., Kelley, M., Goater, C., & Leelesagar, R. *J. Phys.:Condens. Matter*, 2003, **15**, S2323-34.
- 6) Doweidar, H.J. *J. Mat. Sci.*, 1990, **25**, 253-258.
- 7) Shibata, M., Sanchez C., Patel, H., Feller, S., Stark, J., Sumcad, G., & Kasper, J. *J. Non-Cryst. Solids*, 1985, **85**, 29.
- 8) Kodama, M., Matsushita, T., & Kojima, S. *Jpn. J. Appl. Phys.*, 1995, **34** (5B), 2570-74.

- 9) Kodama, M. *J. Mat. Sci.*, 1991, **26** (15), 4048-53.
- 10) Kodama, M. *J. Non-Cryst. Solids*, 1991, **127** (1), 65-74.
- 11) Kodama, M. *J. Am. Ceram. Soc.*, 1991, **74** (10), 2603-09.
- 12) Kodama, M., Hirashima, T., & Matsushita, T. *Phys. Chem. Glasses*, 1993, **34** (4), 129-39.
- 13) Kodama, M., Ono, A., Kojima, S., Feller, S.A., & Affatigato, M. "Borate Anomaly and Anharmonicity in Sodium Borate Glasses." (submitted to *The Proceedings of the 5th International Conference on Borate Glasses, Crystals and Melts*)
- 14) Kodama, M., Iizuka, K., Miyashita, M., Nagai, N., Clarida, W., Feller, S.A., & Affatigato, M. *Glass Techno.*, 2003, **44** (2), 50-8.
- 15) Bowman, H.A., Schoonover, R.M., & Carroll, C.L. *Metrologia*, 1978, **10**, 117.
- 16) Chong, B.C.L., Choo, S.H., Feller, S., Teoh, B., Mathews, O., Khaw, E.J., Feil, D., Chong, K.H., Affatigato, M., Bain, D., Hazen, K., & Farooqui, K. *J. Non-Cryst. Solids*, 1989, **109**, 105-113.

- 17) Kroeker, S.C., Aguiar, P.M., Feller, S.A., & Affatigato M. “Exploring Medium-Range Order in Borate Glasses: New Experimental and Theoretical NMR Approaches.” (submitted to *The Proceedings of the 5th International Conference on Borate Glasses, Crystals and Melts*)
- 18) Clarida, W.J., Berryman, J.R., Affatigato, M., Feller, S.A., Kroeker, S.C., Ash, J., Zwanziger, J.W., Meyer, B., Borsa, F., & Martin, S.W. *Phys. Chem. Glasses*, 2003, **44** (3), 215-7.
- 19) Shannon, R.D. *Acta. Cryst.*, 1976, **A32**, 751.
- 20) Giri, S., Gaebler, C., Helmus, J., Affatigato, M., Feller, S., & Kodama, M. *J. Non-Cryst. Solids*, 2004, **347**, 87-92.
- 21) Greenblatt, S., Bray, P.J. *Phys. Chem. Glasses*, 1967, **8**(5), 190.
- 22) Lower, N.P., McRae, J.L., Feller, H.A., Betzen, A.R., Kapoor, S., Affatigato, M., & Feller, S.A. *J. Non-Cryst. Solids*, 2001, **293-295**, 669-675.
- 23) Doweidar, H. *J. Non-Cryst. Solids*, 1996, **194**, 155-162.

Volume of the f_1 Unit as a Function of Composition

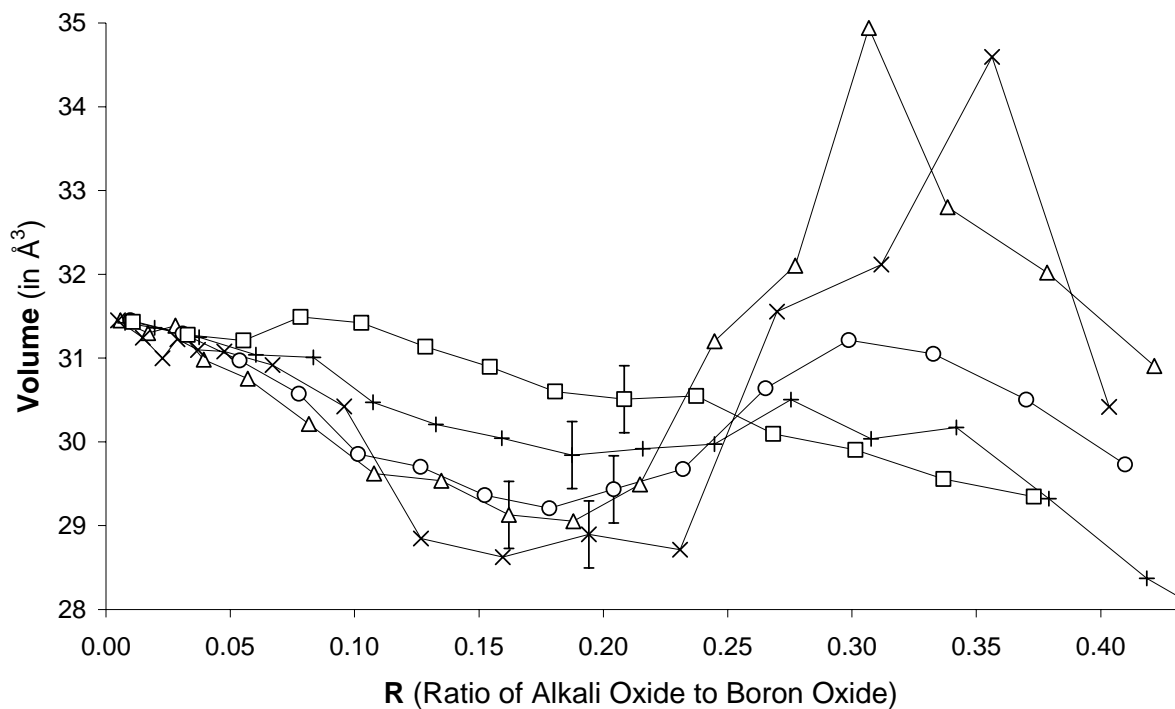


Figure 1: Volume of the f_1 unit as a function of R (ratio of alkali oxide to boron oxide) for the five alkali borate systems. The cesium system is represented by “ Δ ”, rubidium by “ \times ”, potassium by “ \circ ”, sodium by “ $+$ ”, and lithium by “ \square ”. Estimated uncertainty in the volume is $\pm 0.4 \text{ \AA}^3$, represented graphically by the error bars.

Volume of the f_2 Unit as a Function of Composition

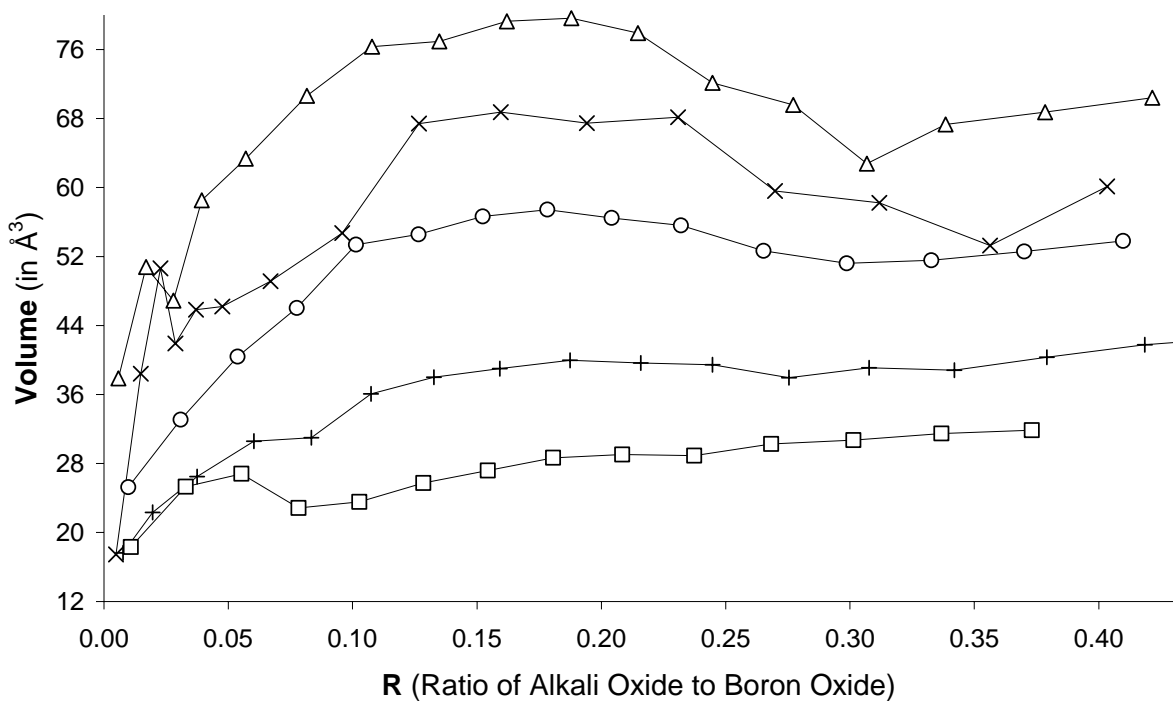


Figure 2: Volume of the f_2 unit as a function of R (ratio of alkali oxide to boron oxide) for the five alkali borate systems. The cesium system is represented by “ Δ ”, rubidium by “ \times ”, potassium by “ \circ ”, sodium by “+”, and lithium by “ \square ”. Estimated uncertainty in the volume is $\pm 0.9 \text{\AA}^3$, approximately the size of the data markers.

Comparison of Best Fit f_2 Unit Volumes to Volume of Alkali Ion

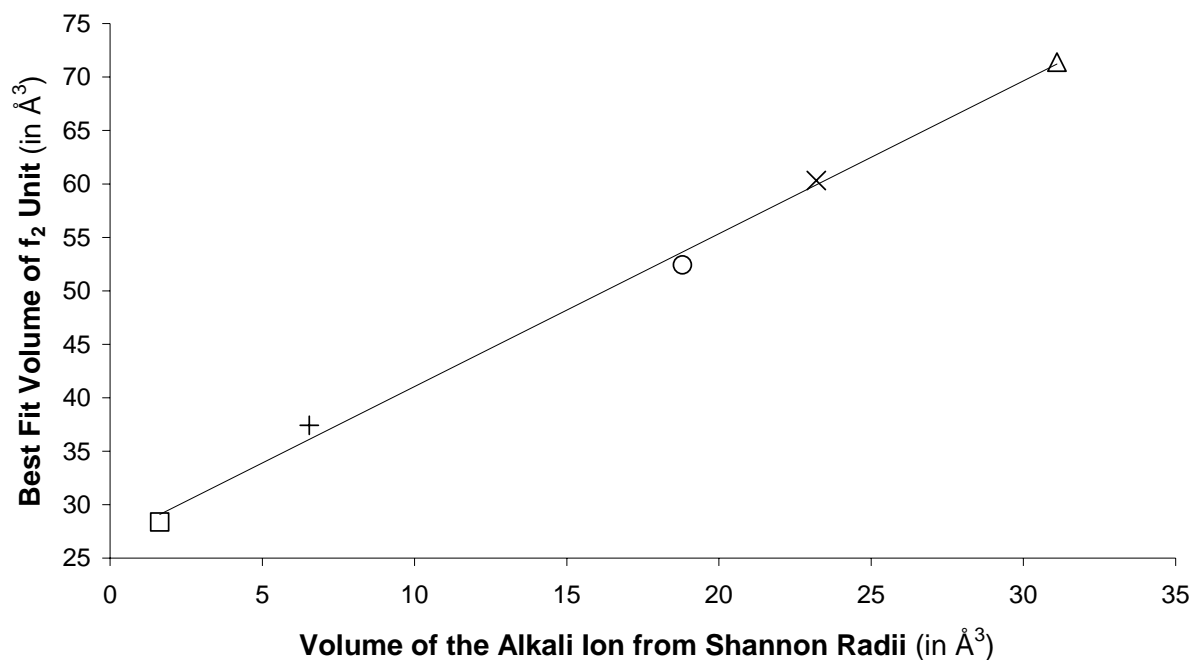


Figure 3: A comparison of the best fit average volume of the f_2 unit over the entire range of available compositions versus the volume of the alkali ion calculated from Shannon radii for the five alkali borate systems. The cesium system is represented by “ Δ ”, rubidium by “ \times ”, potassium by “ \circ ”, sodium by “+”, and lithium by “ \square ”. The equation of the linear fit is given by $y = 1.43 \cdot x + 26.8$, with an R^2 value of 0.997.

Volumes of the f_1 & f_2 Units of Ba-B Compared to Na-B

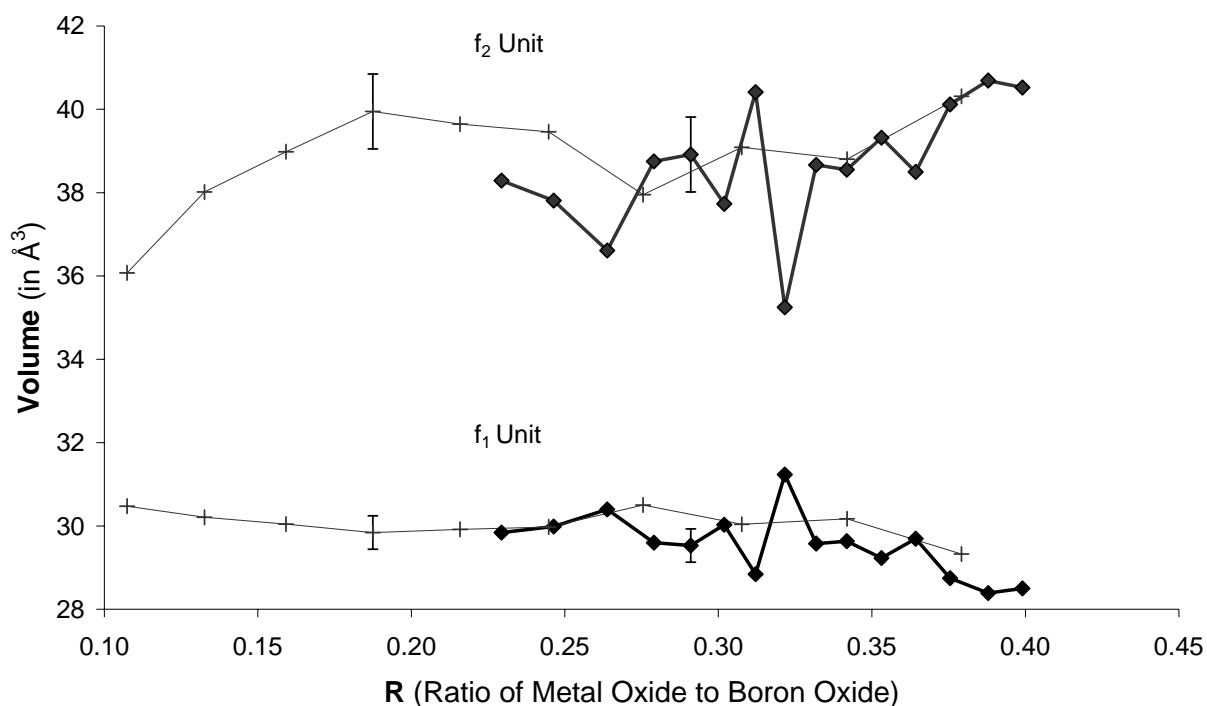


Figure 4: Volumes of the f_1 and f_2 unit as a function of R (ratio of alkali oxide to boron oxide) of barium borates compared to sodium borates. The barium system is represented by “◆”, and sodium by “+”. Estimated uncertainty in the f_1 volumes is $\pm 0.4 \text{ \AA}^3$, and in the f_2 volumes, $\pm 0.9 \text{ \AA}^3$, represented graphically by the error bars.

Volume of f_1 and f_2 Units of Rb and Cs (Extended to $R = 0.6$)

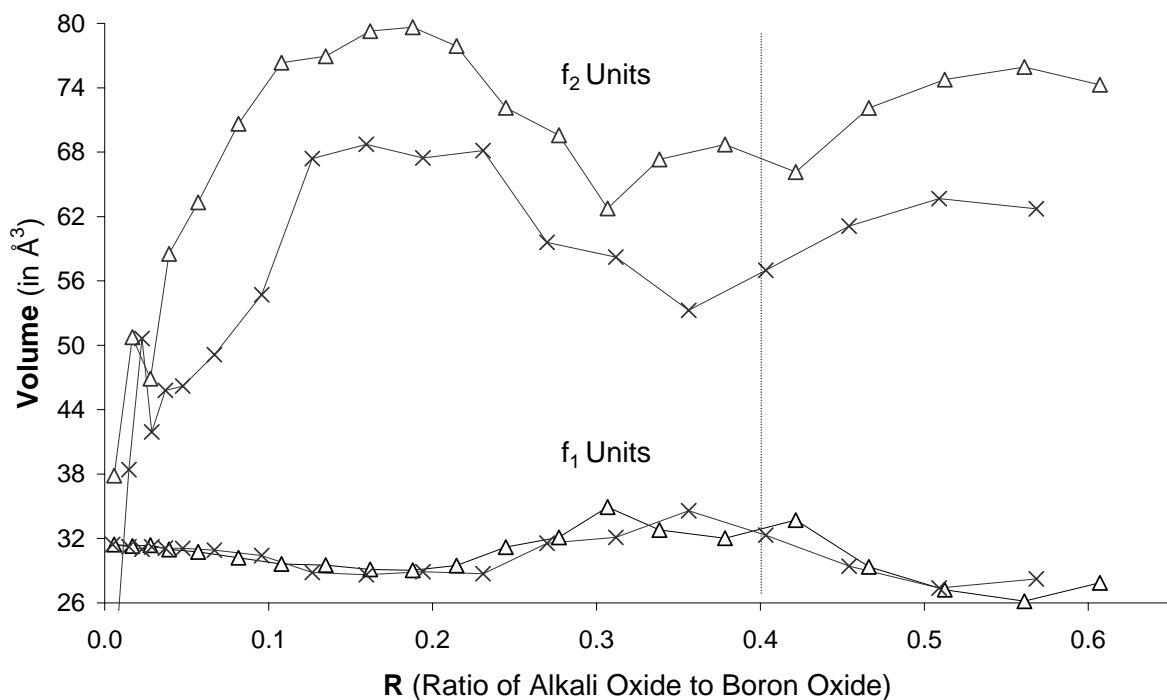


Figure 5: Volumes of the f_1 and f_2 unit as a function of R (ratio of alkali oxide to boron oxide) of cesium borates and rubidium borates, extended to $R = 0.6$. The cesium system is represented by “ Δ ”, and rubidium by “ \times ”. All data points to the right of the vertical dotted line were calculated using the approximation of holding the f_3 unit volume constant. Estimated uncertainty in the f_1 volumes is $\pm 0.4 \text{ \AA}^3$, and in the f_2 volumes, $\pm 0.9 \text{ \AA}^3$, approximately equal to or less than the size of the data markers.