Regression analysis on the amount of tetrahedral boron in borosilicate glasses

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Abstract

Regression analysis was performed to predict the fraction of the four-fold coordinated boron atoms (B4) in the various ternary borosilicate glass systems by using the glass basicity as an explanatory variable. In the analyses, the B4 fraction against the sum of silicon content multiplied by the coefficient *f* and boron content, B4/(B+Si×*f*) was used as an induced variable, and the regression formulae were constructed as a function of the basicity calculated from the glass composition. After the optimization of the coefficient *f*, the regression formulae were successfully obtained for the borosilicate glasses, in which all the correlation coefficients were higher than 0.8.

Introduction

The additivity rule [1] is well known as a simple method to predict the properties and structure of glasses; in general, a property of a glass is expressed by the sum of the additivity factor for each glass constituent. In the case of a binary glass system, a property is approximated by a straight line against the composition. However, the additivity rule is not applicable to some glass systems, such as borate and germanate glasses. Such the nonlinearity between the composition and property found in borate and germanate glasses is well known as borate and germanate anomalies. In these glasses, a characteristic structural change is commonly observed, that is, the change in the coordination numbers of boron and germanium atoms, and the average coordination numbers change non-linearly against the composition. Recently, a novel prediction method [2] has been developed by modifying the additivity rule, where various properties in the database, Interglad [3] were successfully expressed by a multiple regression. Even in the novel method, however, the additivity factors should be determined empirically according to the experimental data. It is hence impossible to expect whether a property of interest will be improved or not when a novel component whose additivity factor has never been given is added to a glass.

Originally, property of a material depends on its structure. It is therefore possible to make an accurate prediction of the glass property if glass structure is estimable from the glass composition. Actually, ab-initio simulations such as molecular dynamics and molecular orbital calculations are applicable to the prediction of glass structure and properties. Even in the ab-initio calculations, however, it is not easy to reproduce the accurate structures in the multicomponent glasses. If there is some sort of prediction method of glass structure which is applicable to the glasses with complex composition, it will be of great benefit in the development of new glasses.

Basicity is a candidate for the dominant factor of glass structure. Aluminum atoms as well as boron and germanium atoms show the change in coordination number according to the glass composition. Various interpretations have been proposed for the change in coordination structures. An interpretation given by

Kawazoe [4] seems to be rational, which is based on a basicity concept proposed by Duffy and Ingram [5]. In the lower basicity glasses, Al atoms occupy octahedral sites, and in the higher basicity glasses, they preferentially enter tetrahedral sites. In general, basicity of oxide glass is interpreted as an ability of electron donation of oxide ions, and oxide ions with higher basicity possess excess electrons. In the glasses with higher basicity, the negative charge of oxide ions is higher, and hence, the positive charge of Al ions is compensated by a small number of oxide ions, resulting in the 4-fold coordination. Miura et al. [6] have compiled the complicated structural changes in borosilicate glasses on the basis of basicity. According to their perspective, there is a basicity region, and a structural group is stably present only in the basicity region. For example, non-bridging oxygen atoms (NBO) in trigonal BO_3 units are formed only in the glasses whose basicity is higher than 0.53.

The glass basicity can be determined from experiments, such as activity of oxide ion, optical absorption and electron spin resonance [7]. Duffy and Ingram [5] proposed a basicity concept based on optical absorption, which was named optical basicity. They also provided a numerical expression of the optical basicity [5]. The basicity calculation requires no experimental data such as density or refractive index, and hence the optical basicity of a glass is estimable directly form the glass composition. In a glass prepared from N kinds of raw materials, N kinds of independent parameters (N–1 indeed) are required to express the glass composition, and in the multicomponent glasses, therefore, it is difficult to examine the compositional dependency of a property. By using a universal criterion such as basicity, all the glasses can be expressed comprehensively by only one variable, and it becomes possible to compare the glasses even in the case with no common constituent.

In the present study, the dependence of glass structure on the basicity was examined in alkali and alkaline-earth ternary borosilicate glasses. The amount of four-fold coordinated boron atoms (B4) was determined from NMR, and the change in the B4 amount against basicity was investigated. Finally, regression analysis was performed by using the basicity as an explanatory variable, aiming for the application of regression analysis to the prediction of glass structure.

Experimental

Glasses in the ternary borosilicate systems $R_2O(MO)$–B_2O_3–SiO_2 containing alkali (R = Li, Na, and K) and alkaline-earth (M = Ca, Sr, and Ba) oxides were prepared by a conventional melt-quenching method. The 10-g batches were melted in a platinum crucible at 1000°C for 30 min to remove carbonates and were melted for 30 more min at 1000 ~ 1300°C for R_2O containing glasses and for 20 more min at 1300 ~ 1550°C for MO containing glasses with the lid of alumina, where the melts were stirred several times to obtain homogeneous specimens. Postannealing was not done in order to avoid phase separation. Inductively coupled plasma analysis was done for some glasses prepared, and the compositional deviation of the cations was less than 5 atomic%.

NMR measurements were carried out at 7.05 T on a Varian UNITYINOVA300 spectrometer. The sample spinning speed at the magic angle to external field was 4.5 kHz. ^{11}B MAS NMR spectra were collected at 78.2 MHz with 1.0-μs pulses and 1.0-s recycle delays. The chemical shift standards used were BPO_4.

Basicity, Λ was calculated from the following equation [5].

$$\begin{cases} \Lambda = \sum_i \dfrac{z_i r_i}{2\gamma_i} \\ \gamma_i = 1.36(\chi_i - 0.26) \end{cases} \qquad (1)$$

where z_i is the oxidation number of the cation i, and r_i is the ionic ratio with respect to the total number of oxides. γ_i is the basicity moderating parameter which is given by the Pauling electronegativity χ_i.

Results and Discussion

Basicity Dependence of the Fraction of Tetrahedral Boron

The fraction of B4, (N_4 ≡ B4/(B3+B4) in the conventional notation) in Na_2O–B_2O_3–SiO_2 system is shown in Figure 1. In the glasses with the same molar ratio SiO_2/B_2O_3, the maxima in N_4 values are commonly observed at basicity $\Lambda \sim 0.55$. A similar trend was also confirmed in the other glass systems. It is therefore concluded that the B4 fraction is dependent on the glass basicity. However, the glasses with the different SiO_2/B_2O_3 ratios indicate the different B4 fraction even at the same basicity. It suggests that single regression is not applicable to the B4 fraction if using the glass basicity as an explanatory variable.

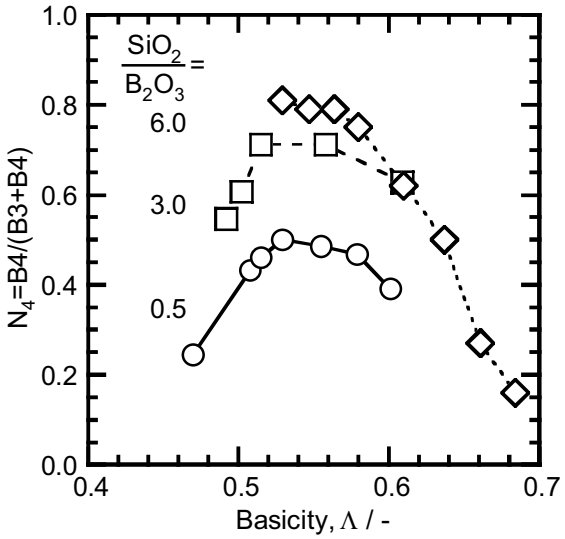

Figure 1: Fraction of four-fold coordinated boron atoms to total boron atoms, N_4 in Na_2O–B_2O_3–SiO_2 system determined from ^{11}B MAS NMR. SiO_2/B_2O_3 indicates the molar ratio in the glass composition.

It is premature to conclude that the basicity does not become the explanatory variable in the regression analyses of glass structure. In Figure 2, the NBO fraction determined from the XPS measurements [6] is plotted as a function of the glass basicity, where the data shown in Fig. 2 were obtained from the same glass specimens used for Fig. 1. Even in the glasses with the different SiO_2/B_2O_3 ratio, one-to-one correlation is recognized between the glass basicity and NBO fraction. At the basicity region $\Lambda > 0.51$, the correlation coefficient R is 0.996, indicating the close correlation between the NBO fraction and basicity. It is notable that the correlation is expressed by a straight line, that is, a first-degree single regression model is applicable to the prediction of NBO fraction in the glasses. Thus, in some structures, the glass basicity is available as an explanatory variable in the first-degree single regression analysis.

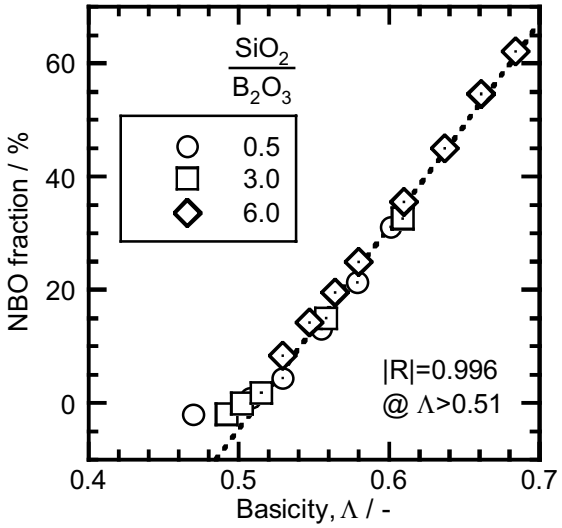

Figure 2: Fraction of non-bridging oxygen, NBO in $Na_2O–B_2O_3–SiO_2$ system determined from XPS [6]. SiO_2/B_2O_3 indicates the molar ratio in the glass composition, and R is the correlation coefficient between the NBO fraction and basicity, Λ shown by the dotted line.

Regression Analyses in $Na_2O–B_2O_3–SiO_2$ System

The structural information directly obtained from the NMR analysis is the relative amount of trigonal and tetrahedral boron atoms. In the borosilicate glasses, however, the glass networks are formed not only by BO_n units but also by SiO_4 units. In a different point of view, therefore, the relative amount of B4 against the total amount of network forming cations instead of boron content was estimated. In the case of the conventional notation, N_4 (Fig. 1), the B4 fraction is apparently higher in the glasses with higher SiO_2/B_2O_3 ratio. As shown in Figure 3, however, the B4 fraction to the total amount of network forming cations is in the reverse order of the B4 fraction shown in Fig. 1.

When the B4 fraction is written as B4/(B+Si×f), where f is the multiplier coefficient for the Si content, the conventional notation of the B4 fraction N_4 is the case at the coefficient $f = 0$ and the fraction of B4 to the total network formers is the case at $f = 1$. As shown in Figs. 1 and 3, the B4 fractions with the same SiO_2/B_2O_3 ratio are in reverse order between the cases at $f = 0$ and 1. Accordingly, it is expected that a correlation independent of SiO_2/B_2O_3 ratio is obtained by adjusting the coefficient f.

Then, the B4 fractions given with the coefficient f were plotted against the glass basicity, and the correlation between the B4 fraction and basicity was approximated by biquadratic polynomial. Furthermore, the coefficient f was optimized by the quasi Newton method so as to obtain the largest correlation coefficient R in the correlation. As shown in Figure 4, the best correlation ($|R| = 0.96$) is obtained at the coefficient $f = 0.274$.

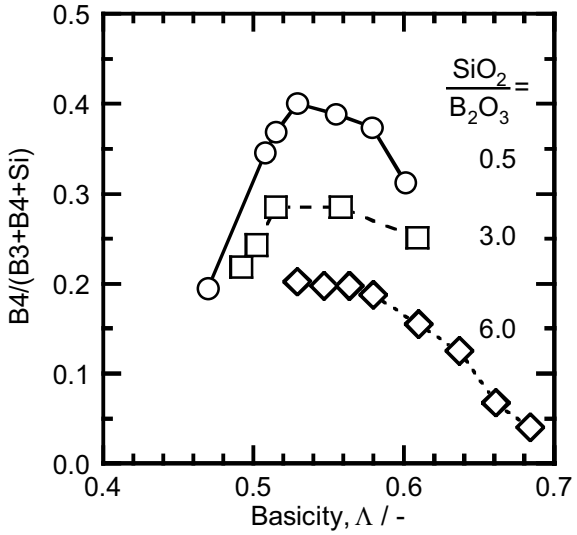

Figure 3: Fraction of four-fold coordinated boron atoms to the total network forming atoms in $Na_2O–B_2O_3–SiO_2$ system. SiO_2/B_2O_3 indicates the molar ratio in the glass composition.

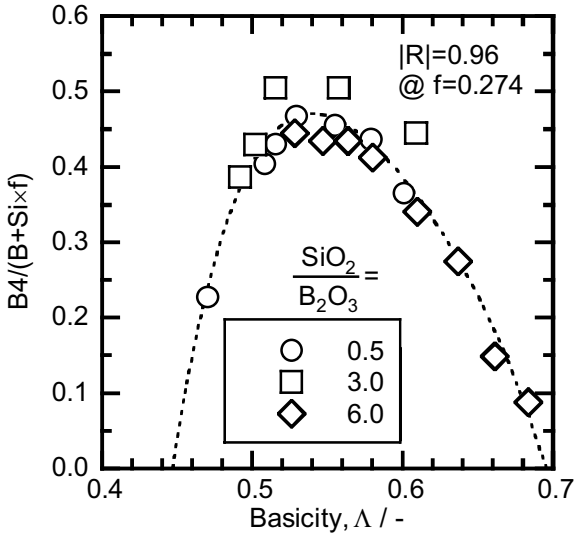

Figure 4: Fraction of four-fold coordinated boron atoms given by B4/(B+Si×*f*) (*f* = 0.274) in $Na_2O–B_2O_3–SiO_2$ system. SiO_2/B_2O_3 indicates the molar ratio in the glass composition, and *R* is the correlation coefficient between the B4 fraction and basicity, *Λ* shown by the dotted line.

As above mentioned, single regression had been hardly applicable to the prediction of the B4 fraction using the glass basicity *Λ* as an explanatory variable, but a little ingenuity introducing the multiplier coefficient *f* has enabled the prediction of the B4 fraction independently of the SiO_2/B_2O_3 ratio. Then, it was examined whether the ingenuity was applicable to the glasses containing other alkali or alkaline-earth oxides.

The glasses used in the present analyses were prepared by the same person, and he measured NMR spectra. The spectral analyses were also done by himself. Therefore, the analytical data used here are at

least precise if not accurate in practice. On the other hand, if assuming a regression analysis based on the reference data given in data books or databases, the analysis should be done based on the data given by the different researchers. Then, the effectiveness of the present method was tested by using the data given in literatures [8-10].

Figures 5a and 5b are the results obtained at $f = 0$ and 0.2259 after optimization, respectively. Low dispersion in the B4 fraction is successfully achieved by introducing the coefficient f. Other information is obtained from Fig. 5; in the basicity regions at $\Lambda < 0.4$ and $\Lambda > 0.7$, the B4 fraction is zero, that is, no tetrahedral BO4 units are present in those regions. As shown in Fig. 2, non-bridging oxygen atoms are only formed at the basicity region at $\Lambda > 0.5$. From these results, it is strongly suggested that structural units in glasses such as BO_4 and NBO are allowed to be present only in the restricted basicity region.

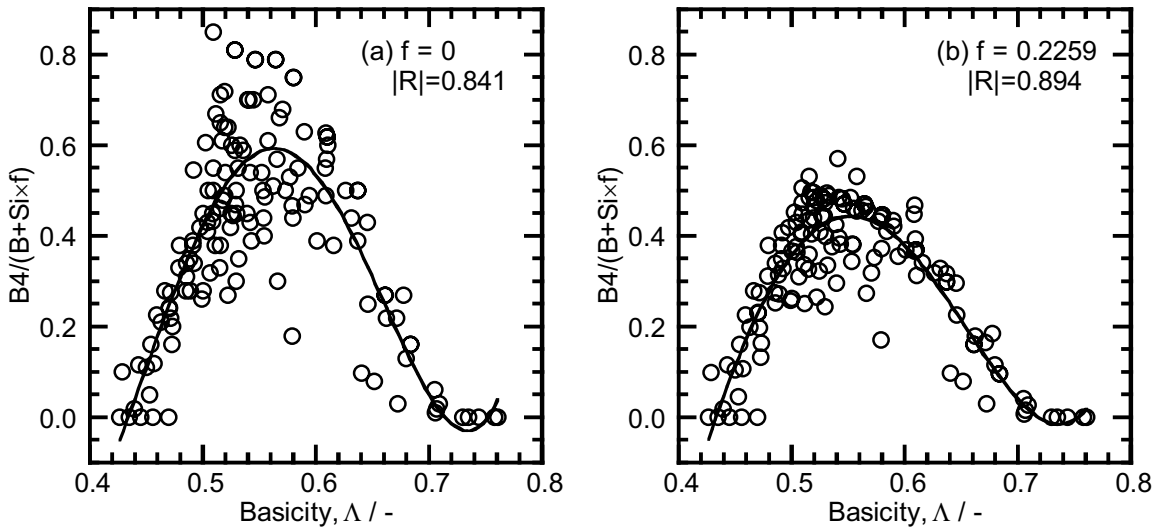

Figure 5: Fraction of four-fold coordinated boron atoms given by B4/(B+Si×f) in $Na_2O–B_2O_3–SiO_2$ system. R is the correlation coefficient between the B4 fraction and basicity Λ shown by the lines. The experimental data were cited from Refs. 8, 9 and 10.

(a) $f = 0$, $y = 665.91\,\Lambda^4 - 1480.2\,\Lambda^3 + 1189.4\,\Lambda^2 - 407.12\,\Lambda + 50.024$

(b) $f = 0.2259$, $y = 287.99\,\Lambda^4 - 596.13\,\Lambda^3 + 430.00\,\Lambda^2 - 123.53\,\Lambda + 11.138$

Regression Analyses in Other Ternary Borosilicate Systems

Zhong et al. [11] reported the B4 fraction in $Li_2O–B_2O_3–SiO_2$ system, and in their report, however, the numerical data were not tabulated. It is difficult to read the accurate values of the B4 fraction from the figure in the printed paper, and hence the results of our measurement were used in the analyses shown below.

The results are shown in Figures 6 and 7 for the glass systems, $Li_2O–B_2O_3–SiO_2$ and $K_2O–B_2O_3–SiO_2$, respectively. The numbers of sample points are fewer than the case of $Na_2O–B_2O_3–SiO_2$ system, and yet good correlations are obtained at $f = 0.0563$ in Li_2O and f $f = 0.2682$ in K_2O containing borosilicate glasses.

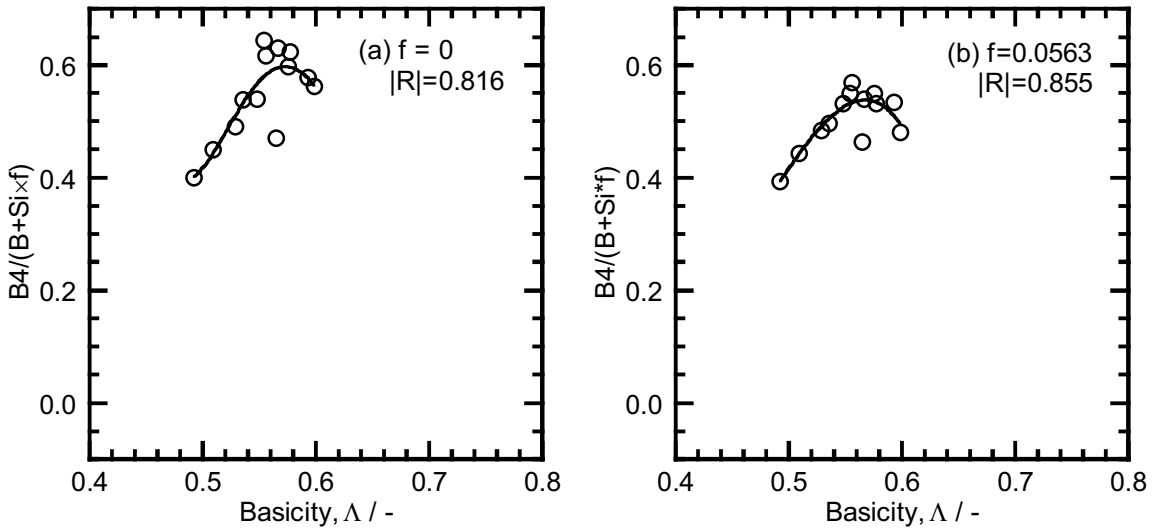

Figure 6: Fraction of four-fold coordinated boron atoms given by B4/(B+Si×*f*) in $Li_2O–B_2O_3–SiO_2$ system. *R* is the correlation coefficient between the B4 fraction and basicity Λ shown by the lines.

(a) $f = 0$, $y = 2986.7\,\Lambda^4 - 6882.5\,\Lambda^3 + 5894.5\,\Lambda^2 - 2223.6\,\Lambda + 312.22$

(b) $f = 0.0563$, $y = -347.19\,\Lambda^4 + 590.71\,\Lambda^3 - 373.05\,\Lambda^2 + 106.52\,\Lambda - 11.72$

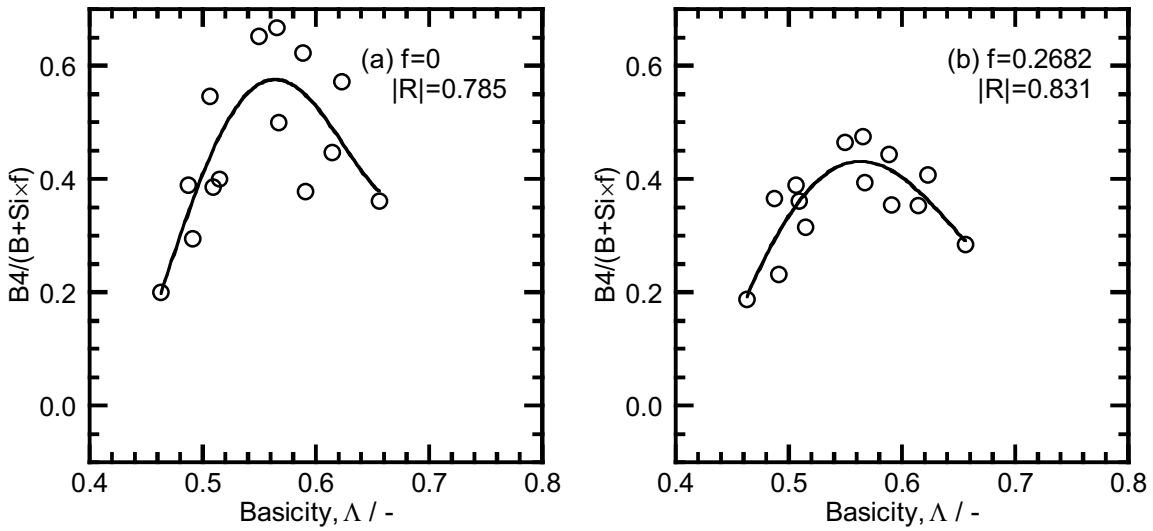

Figure 7: Fraction of four-fold coordinated boron atoms given by B4/(B+Si×*f*) in $K_2O–B_2O_3–SiO_2$ system. *R* is the correlation coefficient between the B4 fraction and basicity Λ shown by the lines.

(a) $f = 0$, $y = 1164.7\,\Lambda^4 - 2546\,\Lambda^3 + 2044.4\,\Lambda^2 - 712.23\,\Lambda + 90.884$

(b) $f = 0.2682$, $y = 316.38\,\Lambda^4 - 673.86\,\Lambda^3 + 513.63\,\Lambda^2 - 163.38\,\Lambda + 18.075$

The results for the glasses containing alkaline-earth oxides, CaO, SrO and BaO are shown in Figures 8, 9 and 10, respectively. At f = 0, the correlation coefficients R are low at around 0.6, and after the exploration of the optimal f values, the correlation coefficient in every system is close to 1.

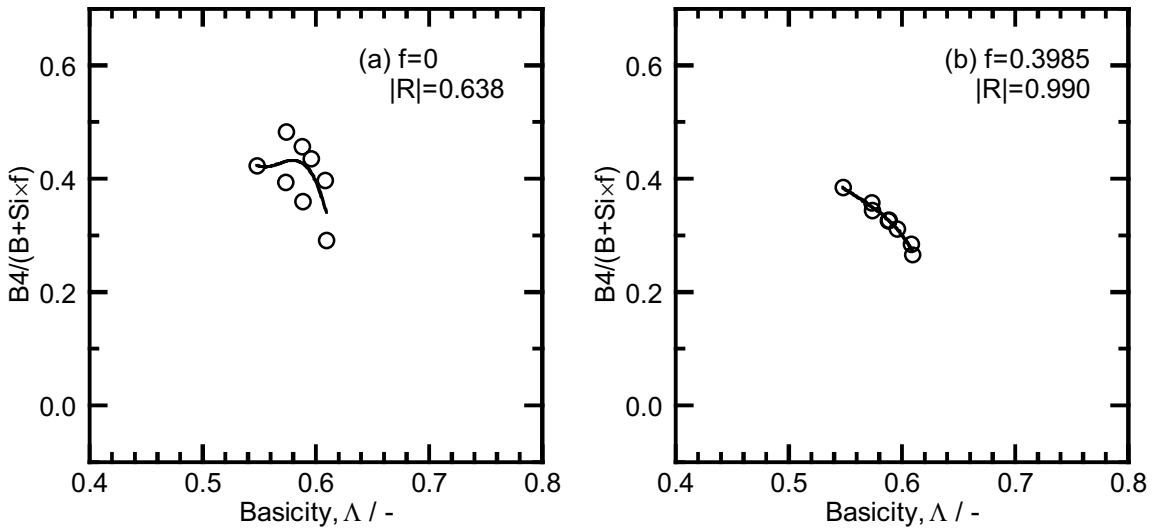

Figure 8: Fraction of four-fold coordinated boron atoms given by B4/(B+Si×f) in $CaO–B_2O_3–SiO_2$ system. R is the correlation coefficient between the B4 fraction and basicity Λ shown by the lines.

(a) $f = 0$, $y = -1601.1\ \Lambda^3 + 2725.8\ \Lambda^2 - 1546\ \Lambda + 292.59$

(b) $f = 0.3985$, $y = -327.93\ \Lambda^3 + 553.7\ \Lambda^2 - 312.91\ \Lambda + 59.547$

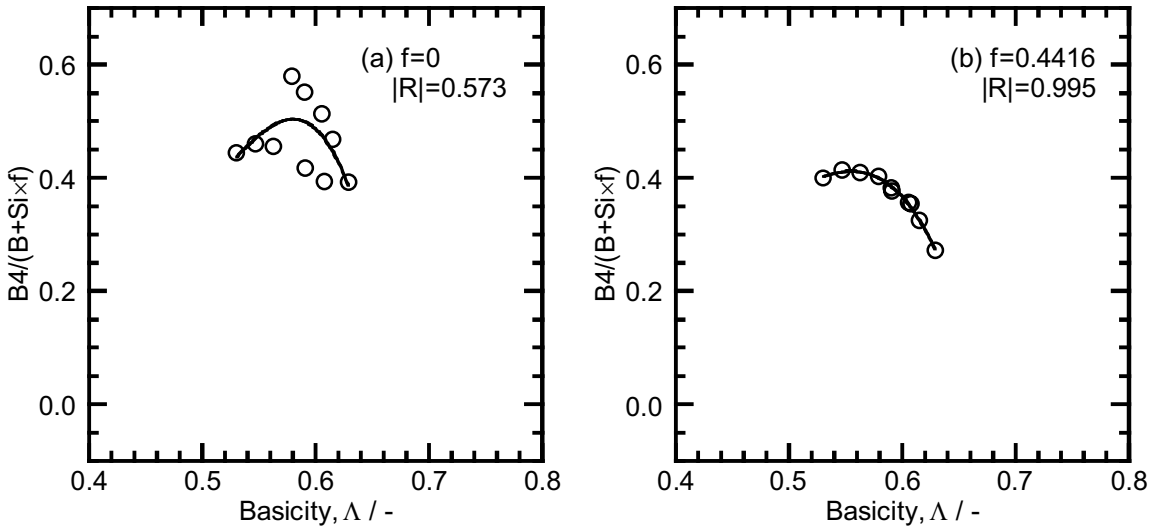

Figure 9: Fraction of four-fold coordinated boron atoms given by B4/(B+Si×f) in $SrO–B_2O_3–SiO_2$ system. R is the correlation coefficient between the B4 fraction and basicity Λ shown by the lines.

(a) $f = 0$, $y = -228.71\ \Lambda^3 + 359.87\ \Lambda^2 - 186.62\ \Lambda + 32.308$

(b) $f = 0.4416$, $y = -99.759\ \Lambda^3 + 148.24\ \Lambda^2 - 72.364\ \Lambda + 11.966$

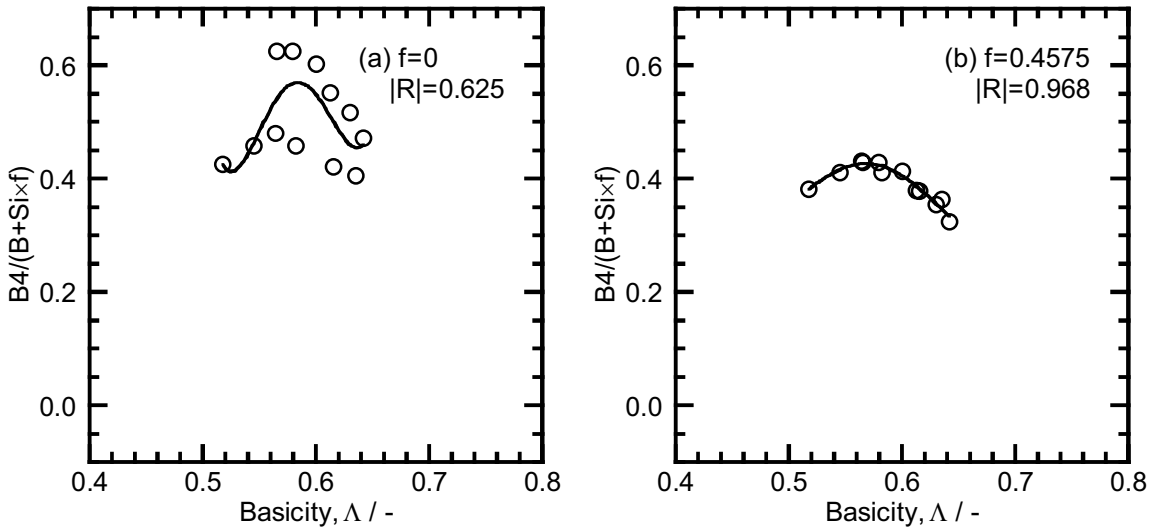

Figure 10: Fraction of four-fold coordinated boron atoms given by B4/(B+Si×*f*) in $BaO–B_2O_3–SiO_2$ system. *R* is the correlation coefficient between the B4 fraction and basicity Λ shown by the lines.

(a) $f = 0$, $y = 14220\,\Lambda^4 - 33095\,\Lambda^3 + 28797\,\Lambda^2 - 11102\,\Lambda + 1600.5$

(b) $f = 0.4575$, $y = 1007.1\,\Lambda^4 - 2305.8\,\Lambda^3 + 1958.6\,\Lambda^2 - 731.4\,\Lambda + 101.7$

The optimal values of the multiplier coefficient *f* for the Si content were individually determined for the tertiary components of alkali and alkaline-earth oxides; $f = 0.0563$ for Li_2O, 0.2259 (0.274) for Na_2O, 0.2682 for K_2O, 0.3985 for CaO, 0.4416 for SrO, and 0.4575 for BaO. Comparing the optimal values, it is found that the alkali oxides give smaller *f* values than the alkaline-earth oxides. It suggests that the alkaline-earth oxides make a larger contribution in the formation of tetrahedral boron atoms than the alkali oxides. As shown in Figure 11, however, when the B4 fractions estimated from the optimal *f*

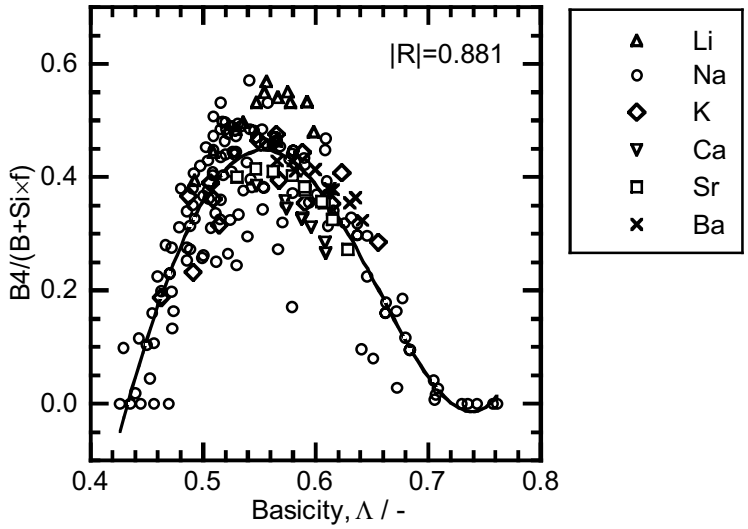

Figure 11: Fraction of four-fold coordinated boron atoms given by B4/(B+Si×*f*) in $R_2O(MO)–B_2O_3–SiO_2$ system. *R* is the correlation coefficient between the B4 fraction and basicity Λ shown by the line.

$y = 283.76\,\Lambda^4 - 588.74\,\Lambda^3 + 425.56\,\Lambda^2 - 122.48\,\Lambda + 11.06$

values are plotted in the same graph, a common correlation is recognized in all the borosilicate systems, and the regression formula gives the high correlation coefficient of 0.881. At this time, the physical or chemical meaning of the coefficient *f* remains obscure. If revealed, however, high-accuracy prediction of the glass structures not only BO_4 units but also other units becomes feasible, and the prediction accuracy of glass properties will also be improved. By incorporating the regressive prediction function into a glass database system, it will be a value-added feature of the database.

Conclusions

Regression analysis was performed to predict the fraction of the four-fold coordinated boron atoms (B4) in the various ternary borosilicate glass systems by using the glass basicity as an explanatory variable. In $Na_2O–B_2O_3–SiO_2$ system, it was confirmed that the B4 fraction, N_4 (≡ B4/B), which has been widely used, was dependent on the glass basicity calculated from the glass composition, but it was also confirmed that the B4 fraction was also dependent on the SiO_2/B_2O_3 molar ratio, indicating that the single regression was not applicable to the B4 fraction if using the glass basicity as an explanatory variable. Then, the B4 fraction against the sum of silicon content multiplied by the coefficient *f* and boron content, B4/(B+Si×*f*) was devised as the induced variable. The coefficient *f* was optimized to obtain the highest correlation coefficient *R* between the basicity and the B4 fraction. Finally, a good correlation of $|R| \sim 0.9$ was successfully established in $Na_2O–B_2O_3–SiO_2$ system.

After the optimization of the coefficient *f*, the regression formulae were successfully obtained for the borosilicate glasses, in which all the correlation coefficients were higher than 0.8.

Acknowledgments

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