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Correlation between basicity and coordination structure in borosilicate glasses

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Various quaternary borosilicate glasses in the general system M_2O–$M'O$–Al_2O_3–B_2O_3–SiO_2 (M=Li, Na or K; M'=Ca, Sr or Ba) were prepared, and the concentration of four-fold coordinated boron (B4) atoms was determined using ^{11}B magic angle spinning NMR. Regression analyses were performed to predict the B4 fraction, in which B4 fraction and glass basicity were used as dependent and independent variables, respectively. Except for Al_2O_3-containing glasses, regression formulae giving high correlation coefficients were successfully obtained by using B4/(B+Si×f) (where f is a tunable coefficient) as the dependent variable. As for the glasses containing Al_2O_3, however, the necessity of a different dependent variable was indicated.

The physical properties of glass change continuously with compositional change, and at the same time, the glass structure also changes, resulting in changes in properties. The additivity rule[1] is useful to predict physical properties of glasses. In a binary glass system, a property of a glass is estimated by a linear approximation connecting both ends of the glass composition. However, in some glasses, such as borate and germanate glasses, properties are not linearly related to composition. In binary alkali borate glasses, the coordination number of boron initially changes from 3 to 4 without forming nonbridging oxygen (NBO) as alkali is added, and then further alkali addition results in a decrease of the coordination number from 4 to 3, accompanied by NBO formation in trigonal BO_3 units. In multicomponent glasses containing B_2O_3 and GeO_2, prediction of glass structure and properties is quite difficult. Multiple regression analysis has been applied to multicomponent glasses to predict the glass properties.[2] As mentioned, the properties of a glass depend on its structure. Therefore, if the structure of a glass is predicted, accurate prediction of glass properties may be achieved, which will contribute to material design of glasses in practical use.

Changes in glass structure are associated with changes in chemical bonding character, that is, electronic states of the glass constituents. In the case of oxide glasses, the electronic states of oxide ions are predominant, because O2p is the main constituent of HOMO (highest occupied molecular orbital) levels. The electronic population of oxide ions is associated with basicity, which is interpreted as an ability of electron donation of oxide ions.[3] It is therefore assumed that glass structure is influenced by basicity. Miura *et al*[4] discussed the structural changes in borosilicate glasses based on a basicity equalisation concept:[3] The borate groups of $BO_{4/2}$ and $BO_{2/2+1}$ units have the same group basicity, λ, of 0·60. As for (Si,B)–O–(Si,B) bridges, λ of bridging oxygens (BOs) is 0·42–0·57, and that of NBOs is 0·79–0·86. According to the basicity equalisation concept,[3] a structural unit having a group basicity λ which is close to a glass basicity Λ is preferentially formed in the glass. In acidic glasses at Λ<0·5, $BO_{4/2}$ units associated with BOs having small λs are stably present, and $BO_{2/2+1}$ units including NBO with large λ are not produced. In basic glasses at Λ>0·6, however, $BO_{2/2+1}$ units are stable, and unstable $BO_{4/2}$ units decrease in concentration with increasing Λ.

A number of numerical expressions for basicity have been proposed. Nanba *et al*[5] concluded that the numerical expression given by Duffy & Ingram[3] was best suited for reproducing the chemical shift of O1s binding energy of oxide glasses. Tateyama *et al*[6] have found good correlations between optical property and the basicity calculated from the equation given by Duffy & Ingram. In our previous study,[7] the correlation between glass structure and basicity was investigated in ternary borosilicate glasses in the general system $M_2O(M'O)$–B_2O_3–SiO_2 (M=Li, Na, K; M'=Ca, Sr, Ba), in which the basicity equation given by Duffy & Ingram was also used. As a result, the fraction of NBOs determined from

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x-ray photoelectron spectroscopy was successfully expressed by a linear function of basicity, and also for the fraction of four-fold coordinated boron (B4) atoms, regression formulae giving high correlation coefficients were successfully obtained.

In the present study, quaternary borosilicate glasses were prepared, and the B4 fraction was determined by using ^{11}B MAS (magic angle spinning) NMR spectrometry. Regression analyses were performed to predict the B4 fraction, in which the B4 fraction and glass basicity calculated from the equation given by Duffy & Ingram[3] were used as dependent and independent variables, respectively. The third and fourth components added to B_2O_3 and SiO_2 were chosen from Al_2O_3, Na_2O, CaO, and BaO, and in total five kinds of quaternary borosilicate glasses were studied by this analysis.

Experimental

The glass compositions investigated are given in Table 1. All the glasses were prepared by a conventional melt quenching method. Batches of 10 g were melted for more than 30 min at 1100–1400°C in a Pt crucible with an alumina lid. Post annealing heat treatment was not done in order to avoid phase separation. Inductively coupled plasma analysis was performed for some of the prepared glasses, and the compositional deviation of the cations was less than 5 at%. Therefore, the nominal composition was used in the basicity calculation.

NMR measurements were carried out at 7·05 T on a Varian Unity Inova 300 spectrometer. ^{11}B MAS NMR spectra were collected at 96·251 MHz with 0·6 μs pulses and 1·0 s recycle delays under the sample spinning speed of 6 kHz at the magic angle to the external field. BPO_4 was used as an external standard for ^{11}B MAS NMR, and the chemical shift of BPO_4 was −3·3 ppm from $BF_3(C_2H_5)_2O$ which was used as a standard reference.

The basicity, Λ, was calculated from the following equations[3]

$$\Lambda = \sum_i \frac{z_i\, r_i}{2\, \gamma_i} \quad (1)$$

$$\gamma_i = 1{\cdot}36(\chi_i - 0{\cdot}26) \quad (2)$$

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.

Table 1. Compositions of the glasses prepared in this study

Glass system	*Composition (molar ratio)*	
$R(x\mathrm{Na_2O}.(1-x)\mathrm{CaO}).B_2O_3.0SiO_2$	x=0·25	R=0·2, 0·3, 0·4, 0·5, 0·6, 0·7
(K=0)	x=0·50	R=0·1, 0·2, 0·3, 0·4, 0·5, 0·6, 0·7
	x=0·75	R=0·1, 0·2, 0·3, 0·4, 0·5, 0·6, 0·7
$R(x\mathrm{Na_2O}.(1-x)\mathrm{CaO}).B_2O_3.1SiO_2$	x=0·25	R=0·25, 0·5, 0·75, 1·0, 1·25, 1·5, 1·75
(K=1)	x=0·50	R=0·25, 0·5, 0·75, 1·0, 1·3, 1·6, 2·0
	x=0·75	R=0·25, 0·5, 0·75, 1·0, 1·3, 1·6, 2·0
$R(x\mathrm{Na_2O}.(1-x)\mathrm{CaO}).B_2O_3.3SiO_2$	x=0·25	R=1·5, 2·0, 2·5, 3·0, 3·5
(K=3)	x=0·50	R=0·5, 1·0, 1·5, 2·0, 2·5, 3·0, 3·5
	x=0·75	R=0·5, 1·0, 1·5, 2·0, 2·5, 3·0, 3·5
$R(x\mathrm{Na_2O}.(1-x)\mathrm{BaO}).B_2O_3.0SiO_2$	x=0·25	R=0·1, 0·25, 0·4, 0·55, 0·7, 0·85
(K=0)	x=0·50	R=0·1, 0·2, 0·3, 0·4, 0·5, 0·6, 0·7
	x=0·75	R=0·1, 0·2, 0·3, 0·4, 0·5, 0·6, 0·7
$R(x\mathrm{Na_2O}.(1-x)\mathrm{BaO}).B_2O_3.1SiO_2$	x=0·25	R=0·25, 0·5, 0·75, 1·0, 1·25, 1·6, 2·0
(K=1)	x=0·50	R=0·25, 0·5, 0·75, 1·0, 1·3, 1·6, 2·0
	x=0·75	R=0·25, 0·5, 0·75, 1·0, 1·3, 1·6, 2·0
$R(x\mathrm{Na_2O}.(1-x)\mathrm{BaO}).B_2O_3.3SiO_2$	x=0·25	R=1·0, 1·5, 2·0, 2·5, 3·0, 3·5
(K=3)	x=0·50	R=0·5, 1·0, 1·5, 2·0, 2·5, 3·0, 3·5
	x=0·75	R=0·5, 1·0, 1·5, 2·0, 2·5, 3·0, 3·5
$R(x\mathrm{CaO}.(1-x)\mathrm{BaO}).B_2O_3.0SiO_2$	x=0·25	R=0·3, 0·4, 0·5, 0·6, 0·7
(K=0)	x=0·50	R=0·3, 0·4, 0·5, 0·6, 0·7
	x=0·75	R=0·3, 0·4, 0·5, 0·6, 0·7
$R(x\mathrm{CaO}.(1-x)\mathrm{BaO}).B_2O_3.1SiO_2$	x=0·25	R=1·0, 1·3, 1·6, 2·0
(K=1)	x=0·50	R=1·0, 1·3, 1·6, 2·0
	x=0·75	R=1·3, 1·6, 2·0
$R(x\mathrm{CaO}.(1-x)\mathrm{BaO}).B_2O_3.3SiO_2$	x=0·25	R=2·0, 2·5, 3·0, 3·5
(K=3)	x=0·50	R=2·0, 2·5, 3·0, 3·5
	x=0·75	R=2·5, 3·0, 3·5
$R\mathrm{Na_2O}.(y\mathrm{B_2O_3}.(1-y)\mathrm{Al_2O_3}).1SiO_2$	R=0·70	y=0·85, 0·70, 0·55, 0·40, 0·25
$R\mathrm{CaO}.(y\mathrm{B_2O_3}.(1-y)\mathrm{Al_2O_3}).1SiO_2$	R=0·70	y=0·70, 0·55, 0·40, 0·25

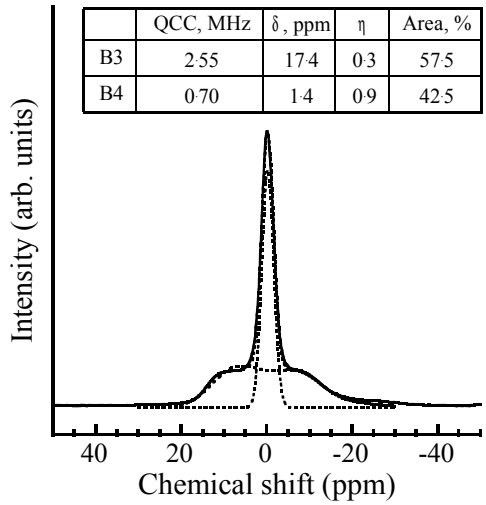

Figure 1. An example of spectral deconvolution of ^{11}B MAS NMR spectrum for 0·75(0·5Na_2O.0·5CaO).B_2O_3.SiO_2 glass (R=0·75, x=0·50, K=1·0). The simulated components and total curve are shown by the dotted lines. The fitting parameters are also shown (QCC: quadrupolar coupling constant; δ: isotropic chemical shift; η: asymmetry parameter)

Results

Compositional dependence of the B4 fraction

Figure 1 shows a typical ^{11}B MAS NMR spectrum for a quaternary borosilicate glass, where the symmetric sharp peak at around 0 ppm is attributed to B4 (i.e. it is attributed to BO_4 units), and the asymmetric broad peak at about 20 to −20 ppm is assigned to B3 (i.e. it is attributed to BO_3 units). Spinning side bands were not observed in this region. The spectra obtained were deconvoluted into the structural components for B3 and B4 species, obtaining the fraction of B4, (N_4≡B4/(B3+B4) in

the conventional notation). The N_4 values estimated in this way have margins of error less than ±0·03.

The fraction of B4 in the Na_2O–CaO–B_2O_3–SiO_2 system is shown in Figure 2. In the glasses with the same network modifier (NWM) content, R=(M_2O+M′O)/B_2O_3, the N_4 value increases with increasing SiO_2 content, K=SiO_2/B_2O_3, and the N_4 value also depends on the NWM mixing ratio, x=M_2O/(M_2O+M′O). As for the series with constant K and x, the addition of NWMs (i.e. an increase in R), results in a transformation from B3 to B4 in the lower R region. With increasing R, the B4 fraction reaches a maximum and then decreases, due to the formation of nonbridging oxygen (NBO) associated with Si and B3. Moreover, the NWM content R at which N_4 shows a maximum is different depending on the SiO_2 content K and NWM mixing ratio, x, indicating that SiO_2 content and NWM species influence the N_4 value.

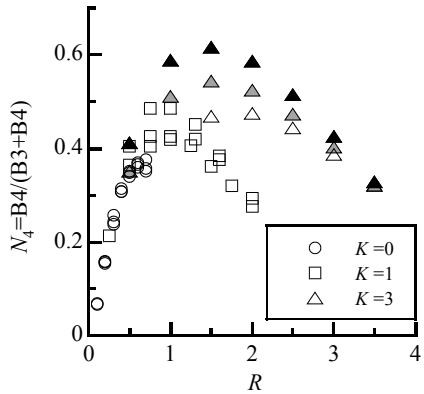

Figure 2. The fraction of four-fold coordinated boron atoms to total boron atoms, N_4 in R(xNa_2O.(1−x)CaO).B_2O_3.KSiO_2 *glasses. The margins of error in N_4 are less than ±0·03. For* K=*3, the glasses with* x=*0·25, 0·50 and 0·75 are indicated by open, gray-coloured and solid markers, respectively*

Regression analysis of the B4 fraction

It is obvious from Figure 2 that the B4 fraction depends on the SiO_2 content, K. In our previous study,[7] the concentration of B4 was expressed as B4/(B+Si×f), and, after optimising the coefficient f, correlations independent of SiO_2 content were successfully obtained. The conventional notation of B4 fraction, N_4=B4/(B3+B4) corresponds to the case with the coefficient f=0, and, in the case with f=1, the denominator, (B+Si×f), means the total amount of network formers (NWFs). In Na_2O or CaO ternary borosilicate glasses,[7] the optimal coefficients f were obtained as 0·226 for Na_2O and 0·399 for CaO, indicating that a fraction of the Si atoms contribute to the formation of tetrahedral BO_4 units.

Then, the B4 concentration expressed with the coefficient f was plotted against glass basicity, and the correlation between the B4 concentration and basicity was approximated by a biquadratic polynomial. Furthermore, the coefficient f was optimised by the quasi-Newton method so as to obtain the largest correlation coefficient, |R|. Figure 3 shows the results for Na_2O–CaO–B_2O_3–SiO_2 glasses. Low dispersion in the B4 fraction is successfully achieved by optimising the coefficient f. It is hence concluded that the notation for B4 concentration expressed using the coefficient f, B4/(B+Si×f), can be used as an dependent variable in the present regression analyses for the quaternary borosilicate glasses. The results of regression analyses for other quaternary borosilicate systems are shown in Figures 4 and 5, for Na_2O–BaO–B_2O_3–SiO_2 and CaO–BaO–B_2O_3–SiO_2 glasses, respectively, in which good correlations are also confirmed after optimising the coefficients, f.

Discussion

Estimation of coefficient f *in quaternary borosilicate glasses*

If the coefficients, f, for multicomponent glass systems were predictable without NMR measurements, it would greatly contribute to the prediction of glass structure. As shown in Figure 3, the optimal coefficient f for the quaternary Na_2O–CaO–B_2O_3–SiO_2 glass is 0·297, which is intermediate between the coefficients f for ternary Na_2O (0·226) and CaO (0·399) borosilicate glasses. Then, the coefficients f for the quaternary glasses were calculated from the follow-

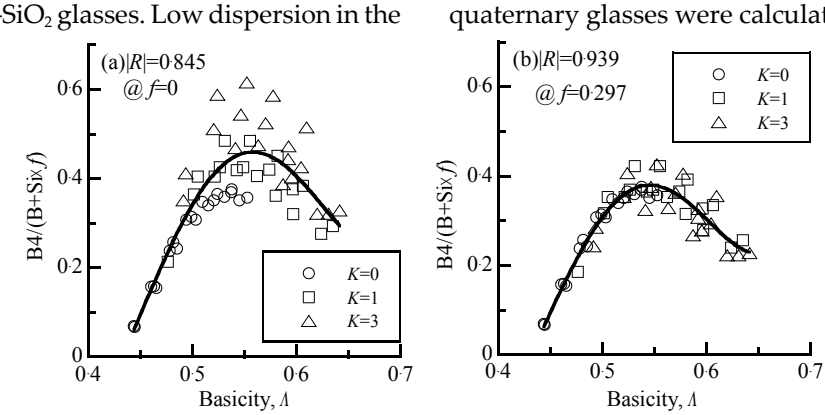

*Figure 3. The fraction of four-fold coordinated boron atoms given by B4/(B+Si×*f*) for the Na_2O–CaO–B_2O_3–SiO_2 system, for* f=*0 and* f=*0·297.* |R| *is the correlation coefficient for the relation between the B4 fraction and basicity, Λ, shown by the lines: (a)* f=*0, y=837·40Λ⁴–1808·5Λ³+1428·5Λ²–486·82Λ+60·361; (b)* f=*0·297, y=996·17Λ⁴–2096·7Λ³+1619·8Λ²–542·21Λ+66·298*

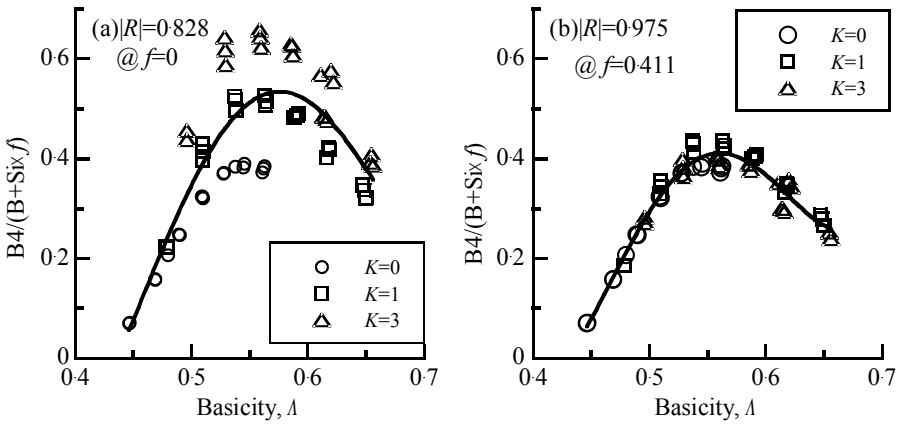

Figure 4. The fraction of four-fold coordinated boron atoms given by B4/(B+Si×f) for the Na_2O–BaO–B_2O_3–SiO_2 system, for f=*0 and* f=*0·411.* |R| *is the correlation coefficient for the relation between the B4 fraction and basicity, Λ, shown by the lines: (a)* f=*0,* y=*493·93Λ⁴–1113·4Λ³+906·94Λ²–314·21Λ+39·016; (b)* f=*0·411,* y=*965·78Λ⁴–2098·8Λ³+1677·1Λ²–582·13Λ+74·084*

ing equation

$$f(\text{mix})=xf(Na_2O)+(1-x)f(\text{CaO}) \quad (3)$$

where $f(Na_2O)$ and $f(\text{CaO})$ are the coefficients obtained for the ternary borosilicate glasses. As shown in Figure 6, high correlation coefficients, $|R|$, are successfully obtained in the quaternary glasses. Compared to the $|R|$ values shown in Figures 3 to 5, the $|R|$ values shown in Figure 6 are slightly reduced, but the difference in $|R|$ is quite small. For example, the $|R|$ value changes from 0·939 to 0·914 in Na_2O–CaO–B_2O_3–SiO_2 glass. It is therefore concluded that the *f* values obtained from the ternary borosilicate glasses are applicable to the estimation of *f* values for multicomponent borosilicate glasses.

Then, is it possible to predict the coefficient *f* for alkali or alkaline earth ternary borosilicate glasses? The character of alkali and alkaline earth ions is often associated with field strength *Z*/*r*, where ionic charge *Z* is divided by ionic radius *r*. Hence, the correlation between the optimal coefficient *f* for ternary borosilicate glasses and field strength *Z*/*r* was examined. As shown in Figure 7, the coefficient *f* decreases with increasing *Z*/*r*, in both the alkali and alkaline earth series. However, the coefficients *f* for the alkaline earth ions are much higher than those for the alkali ions, and a universal relationship is not observed. The chemical or physical meaning of the coefficient *f* is still obscure.

Dependence of the B4 fraction on basicity in aluminoborosilicate glasses

The correlation between B4 fraction and basicity, Λ, for Na_2O–Al_2O_3–B_2O_3–SiO_2 and CaO–Al_2O_3–B_2O_3–SiO_2 glasses is shown in Figure 8. In these glasses, NWM and SiO_2 contents are constant at *R*=0·7 and *K*=1×0, and B_2O_3 is substituted for Al_2O_3. Basicity increases with Al_2O_3 substitution, resulting in a decrease in N_4. As shown in Figures 3 to 6 for alkali and alkaline earth quaternary borosilicate glasses, the maximum B4 fractions are observed at around Λ=0·55. It is hence concluded that the change in coordination structure of boron atoms in aluminoborosilicate glasses is quite different from alkali and alkaline earth borosilicate glasses. In general, Al atoms take coordination numbers of 4 to 6 in glasses, but in the present glasses Al atoms are only in AlO_4 units, which is confirmed from ^{27}Al MAS NMR. As mentioned, the term (B+Si×*f*) in B4/(B+Si×*f*) represents the total amount of NWFs, and

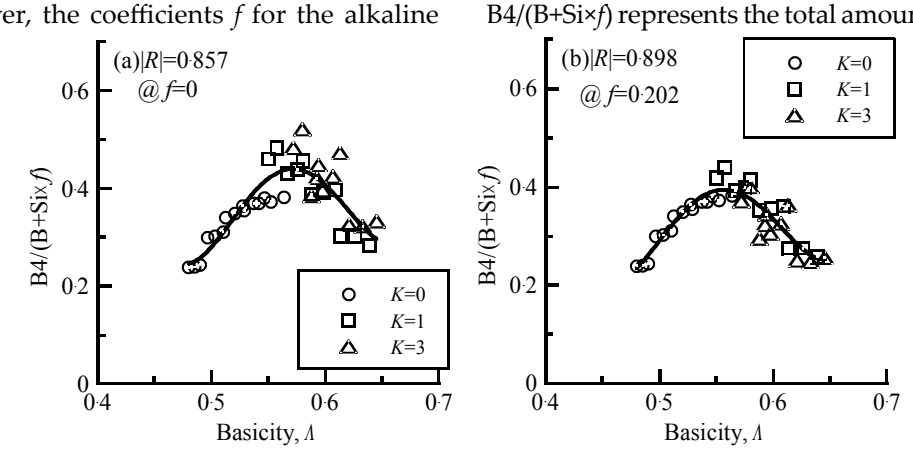

Figure 5. The fraction of four-fold coordinated boron atoms given by B4/(B+Si×f) for the CaO–BaO–B_2O_3–SiO_2 system, for f=*0 and* f=*0·202.* |R| *is the correlation coefficient for the relation between the B4 fraction and basicity, Λ, shown by the lines: (a)* f=*0,* y=*2697·5Λ⁴–6140·6Λ³+5198·6Λ²–1939·3Λ+269·26; (b)* f=*0·202,* y=*2112·9Λ⁴-4678·5Λ³+3847·2Λ²–1391·8Λ+187·14*

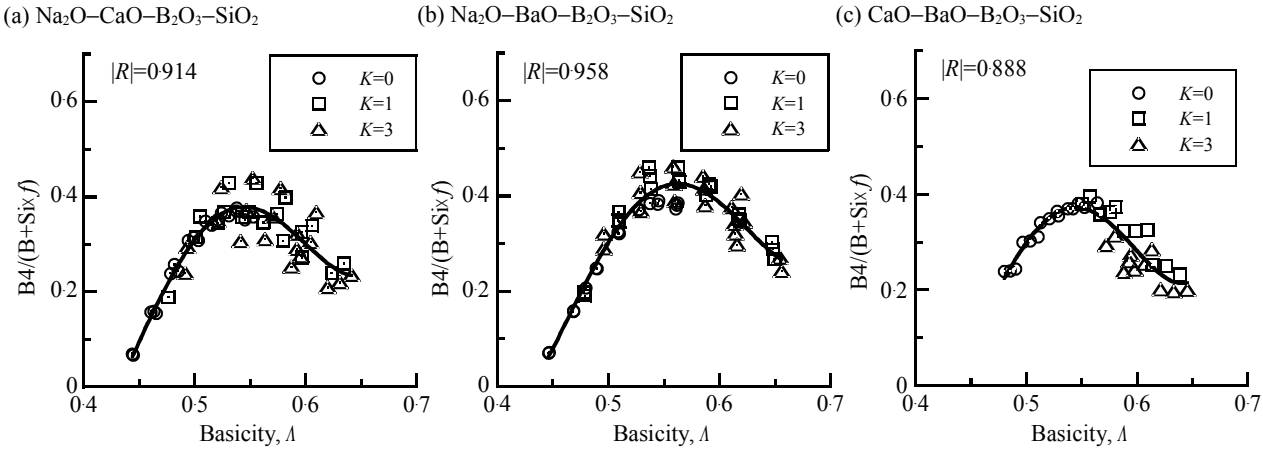

Figure 6. The fraction of four-fold coordinated boron atoms given by B4/(B+Si×f) in quaternary borosilicate glasses, where the coefficients f were obtained from Equation (3). |R| is the correlation coefficient for the relation between the B4 fraction and basicity, Λ, shown by the lines.
(a) $y=1014{\cdot}8\Lambda^4-2128{\cdot}0\Lambda^3+1638{\cdot}1\Lambda^2-546{\cdot}37\Lambda+66{\cdot}555$; *(b)* $y=827{\cdot}66\Lambda^4-1802{\cdot}0\Lambda^3+1438{\cdot}5\Lambda^2-497{\cdot}06\Lambda+62{\cdot}727$
(c) $y=1516{\cdot}0\Lambda^4-3231{\cdot}9\Lambda^3+2544{\cdot}9\Lambda^2-875{\cdot}73\Lambda+111{\cdot}19$

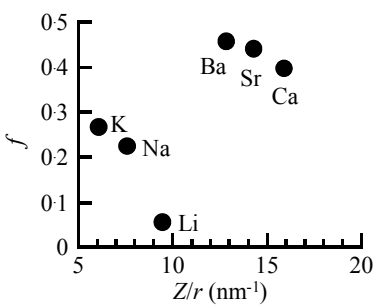

Figure 7. Field strength, Z/r and the optimal coefficient f in B4/(B+Si×f) for the ternary borosilicate glasses[7] (Z and r indicate ionic charge and radius, respectively)

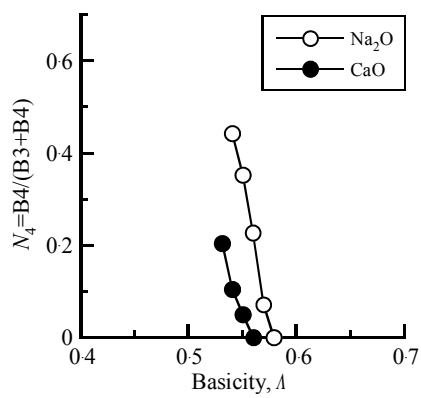

Figure 8. Fraction of four-fold coordinated boron atoms to total boron atoms, N_4 in the Na_2O–Al_2O_3–B_2O_3–SiO_2 and CaO–Al_2O_3–B_2O_3–SiO_2 systems

hence B4/(B+Si×*f*+Al×*g*) is expected as the dependent variable in the present aluminoborosilicate glasses. However, a satisfactory result was not obtained, and hence a different expression for the B4 fraction is required in the case of aluminoborosilicate glasses.

Conclusions

Quaternary borosilicate glasses containing Na_2O, CaO, BaO and Al_2O_3 were prepared, and the concentration of four-fold coordinated boron (B4) atoms was determined by using ^{11}B MAS NMR. Regression analyses were performed to predict the B4 fraction, in which the B4 fraction and glass basicity were used as the dependent and independent variables, respectively. The B4 fraction, expressed as B4/(B+Si×*f*), was used as the dependent variable, obtaining high correlation coefficients after optimisation of the coefficients, *f*, in the quaternary glass systems containing Na_2O, CaO and BaO. High correlation coefficients were also obtained by averaging the coefficients *f* for ternary borosilicate glasses. As for the glasses containing Al_2O_3, however, the necessity of a different dependent variable was indicated.

Acknowledgments

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