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Alkali distribution in borosilicate glasses

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The alkali distribution in borosilicate glass has been discussed on the basis of the different quantities obtained by various experimental methods. The NBO fraction was chosen as a common quantity for evaluating the alkali distribution models. The NBO fractions in sodium borosilicate glasses were estimated from ^{11}B and ^{29}Si NMR as well as XPS. However, the best model was not found among the existing models. The amounts of sodium oxide consumed for the NBO formation in borate and silicate networks and for the formation of BO_4 units were separately estimated from the ^{11}B and ^{29}Si NMR data. A new trend was found in the alkali distribution suggesting the possibility for a new universal distribution model.

Borosilicate glass consists of borate and silicate networks formed by BO_3 and SiO_4 units, and the addition of network modifiers such as alkali and alkaline earth oxides to the glass leads to complicated structural changes. When alkali ions are associated with a silicate network, nonbridging oxygens (NBOs) are formed in the network. When associated with a borate network, fourfold coordinated borons (B4) and NBOs are produced in the borate network. Hence, the amount of the structural species present in the glass is dependent on the amount of the alkali ions associated with silicate and borate networks. Several alkali distribution models have been proposed for alkali borosilicate glasses, in which the glass composition has been commonly represented as $R\mathrm{R_2O.B_2O_3}.K\mathrm{SiO_2}$, where R and K denote the molar ratios, $R=\mathrm{R_2O/B_2O_3}$ and $K=\mathrm{SiO_2/B_2O_3}$. Dell *et al*(1) described the fraction of borons having various coordination structures determined from ^{11}B NMR, in which they assumed macroscopic structural units such as reedmergnerite and diborate groups in the glasses. Zhong *et al*(2) also described the boron fractions given from ^{11}B NMR and their assumption is, however, quite different from that of Dell *et al.*(1) It was assumed in the Zhong model(2) that alkali ions were distributed only within a borate network below the critical $\mathrm{R_2O}$ content, R_0 and for $R>R_0$. However, alkali ions were proportionally distributed within the borate $1/(1+K)$ and silicate $K/(1+K)$ networks. The optimum R_0 value was determined in every K-family of glasses. Martin *et al*(3–5) performed ^{29}Si MAS-NMR measurements, the chemical shift being described on the basis of the Zhong model. However, the optimum R_0 values derived from ^{29}Si and ^{11}B NMR were different from one another.(3) Recently Miura *et al*(6) proposed a new alkali distribution model on the basis of XPS and an appropriate acid–base concept. They also introduced a critical $\mathrm{R_2O}$ content, R_c, assuming the alkali distribution that for $R<R_c$ alkali oxides distributed within the borate network were consumed only in the formation of tetrahedral BO_4 units, and NBOs associated with borate network were produced only after exceeding R_c. In the Miura model, furthermore, alkali ions are differently distributed between borate and silicate networks, where the alkali distribution coefficient, α is introduced to represent the $\mathrm{R_2O}$ content associated with borate and silicate networks. The amount of $\mathrm{R_2O}$ associated with silicate network, R_{Si}, is given by

$$R_{\mathrm{Si}}=\begin{cases}\alpha R & \text{for } R\le R_c\\ (R-R_c)K/(1+K)+\alpha R_c & \text{for } R_c\le R\end{cases} \qquad (1)$$

The coefficient α was optimised to reproduce the NBO fraction evaluated from XPS measurements. The α value so-determined seemed to be in good agreement with the relative amount of Si–O–Si bonds in a $\mathrm{B_2O_3}.K\mathrm{SiO_2}$ glass, suggesting that alkali oxides added to the glass were preferentially consumed in breaking Si–O–Si bonds. In the case $\alpha=0$, Equation (1) is identical to the Zhong model. The physical meaning of R_c is, however, quite different between the Zhong and Miura models, that is, R_c is the critical $\mathrm{R_2O}$ content for the formation of NBO in silicate network in the Zhong model and for the NBO formation in borate network in the Miura model.

These alkali distribution models are evaluated on the basis of different experiments and physical quantities, that is, the Dell and Zhong models are commonly based on the fractions of borons with various coordination structures estimated from ^{11}B NMR, the Martin model is derived from the chemical shift in ^{29}Si MAS-NMR and the Miura model is derived for the NBO fraction determined with XPS. If a common quantity is chosen, it will be possible to compare the models without prejudice. In the present study, the amount of NBO was chosen as a common quantity to review the alkali distribution models.

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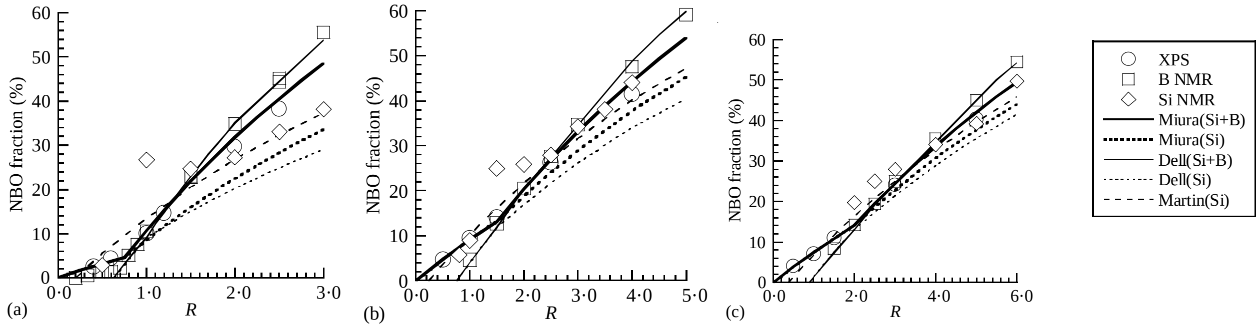

Figure 1(a–c). *Fraction of NBO in $RNa_2O.B_2O_3.KSiO_2$ glasses determined from the experiments (XPS,(6) ^{11}B NMR(1,7) and ^{29}Si MAS-NMR(8)) and the models (Miura,(6) Dell(1) and Martin(4)). (Si+B) represents the fraction of total NBO in the glass and (Si) indicates the fraction of NBO only in the silicate network: (a) $K= 2{\cdot}0$; (b) $K=4{\cdot}0$; (c) $K=6{\cdot}0$*

Evaluation of NBO fraction

In borosilicate glasses, alkali oxides are consumed to produce B4 and NBO. If we assume that BO_4 tetrahedra have no NBO, NBO should be included in either BO_3 triangles or SiO_4 tetrahedra. If such is the case, we can evaluate the amount of NBO from the fraction of fourfold coordinated borons, N_4, according to the following procedures.

1. 1 mole of R_2O forms 2 moles of BO_4 unit

$$2BO_{3/2}+R_2O\rightarrow 2BO_{4/2}$$

Then, when R_{B4} moles of R_2O are consumed to form BO_4 units, $2R_{B4}$ moles of B4 will be produced. An $RR_2O.B_2O_3.KSiO_2$ glass contains 2 moles of B, and N_4 will hence be given by

$$N_4=2R_{B4}/2=R_{B4} \tag{2}$$

2. 1 mole of R_2O forms 2 moles of NBO.

$$(Si–O–Si)+R_2O\rightarrow 2(Si–O\cdots R)$$

$$(B–O–B) + R_2O\rightarrow 2(B–O\cdots R)$$

Then, when R_{Si} and R_{B3} moles of R_2O are consumed to produce NBO in the silicate and borate networks, respectively, $2R_{Si}$ and $2R_{B3}$ moles of NBO will be produced.

3. Let us assume that R_B moles of R_2O are associated with the borate network. R_{B4} and R_{B3} moles of R_2O are consumed to produce BO_4 and NBO, respectively. Here, $R_B=R_{B3}+R_{B4}$ and $N_4=R_{B4}$ from Equation (2) so that we can obtain $R_{B3}=R_B–N_4$. Consequently, $2R_{Si}$ and $2R_{B3}= 2(R_B–N_4)$ moles of NBOs will be produced, and the total amount of NBO in the glass will be $2R_{Si}+2(R_B–N_4)= 2R–2N_4$, where $R=R_{Si}+R_B$.

4. Thus, the total amount of NBO formed in the glass is independent of alkali distribution and it depends only on N_4, that is, the fraction of fourfold borons. Finally, the NBO fraction in the glass, f(NBO) is given by

$$f(NBO)=(2R–2N_4)/(R+3+2K) \tag{3}$$

According to the equation, we can estimate the NBO fraction both from experiments and models.

In XPS analysis, the NBO fraction can be obtained directly from the separation of O1s signal into BO and NBO components, and the further separation such as NBO in borate and silicate networks, however, would not be useful.(6) We can experimentally obtain the N_4 value from boron NMR, but the alkali distribution, R_B, cannot be determined from boron NMR experiments. Assuming that R_{B3}/R_B is proportional to R_B, Zhong *et al*(2) evaluated R_B from ^{11}B NMR, but the assumption is not valid. Silicon NMR is probably the only method that can experimentally determine the alkali distribution, R_{Si}. The amount of NBO in the silicate network can be estimated from the Q_n distribution obtained from silicon NMR, but no information is given from silicon NMR as for the NBO fraction in borate network. Full information on the alkali distribution will be provided with the combination of B and Si NMR experiments.

In the present paper, the experimental data for $RNa_2O.B_2O_3.KSiO_2$ glasses were collected from the literature, XPS reported by Miura *et al*,(6) ^{11}B NMR by Dell *et al*(1) and Yun & Bray(7) and ^{29}Si-MAS NMR by Bhasin *et al*,(8) evaluating the NBO fraction.

NBO fractions evaluated from experiments and models

The NBO fractions evaluated from the various methods are summarised in Figure 1 for the glasses, $RNa_2O.B_2O_3.KSiO_2$ ($K=2{\cdot}0$, $4{\cdot}0$ and $6{\cdot}0$), in which the NBO fractions evaluated from the experimental data are indicated by the markers and those from the models are shown by the lines. As mentioned above, the amount of NBO estimated from XPS or boron NMR should be the total amount of NBO in a glass. In these experiments NBOs in BO_3 and SiO_4 units are indistinguishable. On the other hand, we can evaluate the amount of NBO only in SiO_4 units from the Q_n distribution obtained by silicon NMR. As also described above, R moles of Na_2O are divided into R_{Si} and R_B moles, being distributed within the silicate and borate networks, respectively. Therefore, the fraction of NBO in SiO_4 units must not exceed the total NBO fraction. In Figure 1 some points obtained from silicon NMR exceed the points from XPS and boron NMR. Apart from that, the difference in the NBO fraction between the experiments is quite small, since NBO in SiO_4 units is the predominant species in these higher K-family glasses. If the Q_n distribution in the smaller K-family glasses such as $K=0{\cdot}5$ were available, the difference from silicon NMR would be more obvious.

In the alkali distribution models proposed by Dell *et al*(1), Zhong *et al*(2) and Miura *et al*,(6) the amounts

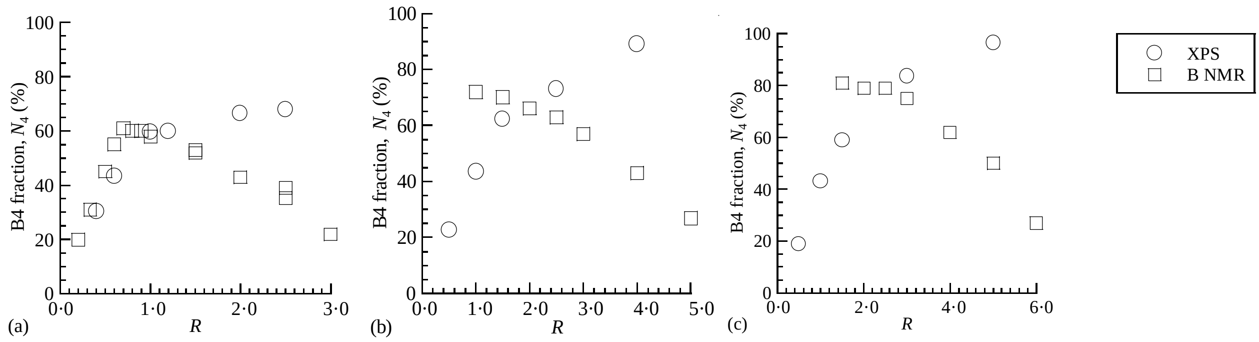

Figure 2(a–c). *Fraction of fourfold coordinated boron, N_4 in $RNa_2O.B_2O_3.KSiO_2$ glasses determined from the XPS(6) and ^{11}B NMR(1,7) experiments: (a) K=2·0; (b) K=4·0; (c) K=6·0*

of Na_2O distributed within the silicate and borate networks, R_{Si} and R_B, are separately predicted. In the Zhong model,(2) however, an arbitrary assumption is required in the prediction of the total NBO amount. Martin *et al*(4) adopted the same expression of the Zhong model, but they have applied the expression only to the R_{Si} prediction. The Dell,(1) Martin(4) and Miura(6) models are chosen to compare the NBO fractions. The NBO fractions predicted from these models are in good agreement with the respective experimental data with the same experimental origin. Unfortunately, it is hard to judge the best model from Figure 1.

As shown in Figure 1, the difference in the experimental NBO fraction between XPS and boron NMR is small, while in the higher R regions, the NBO fraction from boron NMR is somewhat higher than that from XPS. According to Equation (3), the fraction of fourfold boron, N_4 is inversely estimated from the total NBO fraction. The N_4 values were calculated from the experimental NBO fraction obtained from XPS. The result is shown in Figure 2 together with the experimental N_4 data reported elsewhere.(1,7) As compared with the NBO fraction, the difference in N_4 is quite obvious, particularly in the higher R regions. These evaluations are based on two assumptions, that the tetrahedral BO_4 units include no NBO and the NBO component separated from O1s signal contains all NBOs both in BO_3 and SiO_4 units. These assumptions imply the consistency between the results of XPS and boron NMR. The inconsistency shown in Figure 2 suggests that one or both the assumptions are inapplicable in the present case. The basicity of a BO_4 unit with one NBO is 0·71, which is much higher than the average basicity of the glass matrix, 0·44–0·65.(6) Therefore, it is reasonable to assume that the BO_4 units in the present glasses include no NBOs, and NBOs in borate network are preferentially bound to threefold borons.

It should also be noted in Figure 1 that the NBO fractions obtained from XPS are much closer to those from silicon NMR rather than boron NMR, excepting the glasses in which silicon NMR shows the highest NBO fraction. It leads to another interpretation in the NBO component separated from O1s XPS signal; NBOs only in the SiO_4 units contribute to the NBO component and NBOs in BO_3 units are put into the BO component. Hsieh *et al*(9) separated the O1s XPS signal for sodium borosilicate glasses into three components, bridging oxygen, B–O–Na and Si–O–Na, concluding that the area fraction of these components follows the Dell model. As shown in Figure 1, however, the NBO fraction obtained from XPS(6) shows the fraction of NBO in SiO_4 units much higher than predicted from the Dell model. Chemical species in the borosilicate glasses are quite complicated; as for BO, B3–O–B3 (λ= 0·42), B3–O–Si (0·45), Si–O–Si (0·48), B3–O–B4 (0·49), B4–O–Si (0·52) and B4–O–B4 (0·57) are present, and as for NBO, B3–O–Na (0·79) and Si–O–Na (0·81) are present, where λ indicates the theoretical microscopic optical basicity of individual oxide ions.(10) The difference in basicity of NBOs is too small to separate O1s XPS signal into B3–O–Na and Si–O–Na components. Furthermore, it is expected in the present glasses that electrons on oxide ions easily delocalise through vacant $B2p_z$ orbital in planer BO_3 triangles. The electron delocalisation as well as the structural diversity probably brings about great difficulty in O1s peak separation.

Alkali distribution in sodium borosilicate glass

As already mentioned, full information for the alkali distribution is expected from B and Si NMR experiments; the amount of alkali oxide consumed in producing the BO_4 unit, R_{B4} is identical with the fraction of fourfold coordinated boron, N_4, the amount of R_2O distributed to silicate network, R_{Si} is given by ½×´(the amount of NBO in SiO_4 units), and the residual R_2O, $R-R_{B4}-R_{Si}=R_{B3}$ is consumed to form NBO in BO_3 units, where the assumption that BO_4 units include no NBO is still valid. The amounts of R_{B3}, R_{B4} and R_{Si} for the glasses, $RNa_2O.B_2O_3.KSiO_2$ (K=2·0, 4·0 and 6·0) are estimated from the experiments of ^{11}B NMR(1,7) and ^{29}Si MAS-NMR(8) and the relative amounts to the total Na_2O content, R are plotted in Figure 3, where some Si NMR data giving higher NBO fraction than B NMR are excluded. The relative amount of Na_2O consumed to form BO_4 units, R_{B4}/R decreases continuously with increasing R. The relative amount of Na_2O distributed within the silicate network, R_{Si}/R is almost constant in higher R regions. The relative amount of Na_2O consumed to form NBO in BO_3 units, R_{B3}/R has a critical threshold, and R_{B3}/R increases monotonically above the threshold. Consequently, each K family glasses are divided into three R regions, being defined by two critical R values, R_{C1} and R_{C2}. At $R<R_{C1}$, R_{B4}/R

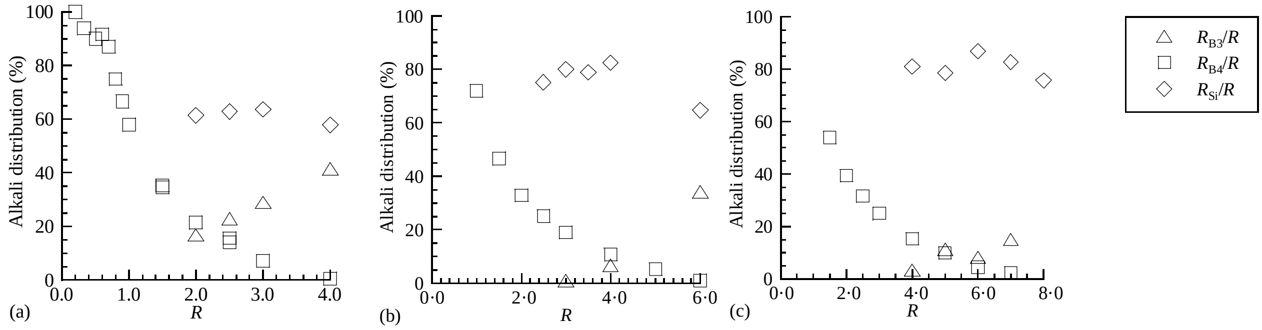

Figure 3(a–c). *Relative amount of Na_2O distributed to BO_3, BO_4 and SiO_4 units in $RNa_2O.B_2O_3.KSiO_2$ glasses: (a) K=2·0, (b) K=4·0; (c) K=6·0*

decreases and R_{Si}/R increases with increasing R, and no Na_2O is consumed to produce NBO in BO_3 units (R_{B3}/R=0) until R reaches R_{C1}. At $R_{C1}<R<R_{C2}$, R_{Si}/R is constant so that the relative amount of Na_2O distributed to borate network, $R_B(=R_{B3}+R_{B4})/R$ is also constant. In that region, R_{B4}/R still decreases and R_{B3}/R increases with increasing R. At $R_{C2}<R$, little structural information is available. It is expected in the glasses that there are no BO_4 units (R_{B4}/R=0) and R_{B3}/R still increases from the previous region and R_{Si}/R turns into decreasing.

As mentioned, some Si NMR data are omitted from Figure 3 because $R_{Si}+R_{B4}$ exceeds the total Na_2O amount R. The strange results are seen at small R regions, which is probably due to the overestimation of NBO amount in the Si NMR analysis, i.e. part of BO in B–O–Si bonds might be assigned to NBO in Si NMR. As shown in the previous section, BO in the B4–O–Si bond (λ = 0·52) surely possesses higher basicity than BO in Si–O–Si (0·48), but the difference in basicity is much smaller than that from NBO in Si–O–Na (0·81). Therefore, it is hard to explain the overestimation on the basis of the simple basicity concept. Nevertheless, it is supposed that in electronic population there is no great difference between BO in B4–O–Si and NBO in Si–O–Na. According to Miura *et al*,(6) NBOs in SiO_4 units donate lone pair electrons to the vacant $B2p_z$ orbital in the neighbouring BO_3 units, and they turn into BOs forming B4–O–Si bonds in the end. The electronic delocalisation through B4–O bonds is much less than that through B3–O bonds due to the lower π-bonding character of B4–O, and it is therefore expected that BOs in the B4–O–Si bonds formed in this way possess electrons similar to the NBOs in Si–O–Na units and they have been assigned to NBO in Si NMR. Probably, it is also the case in XPS. As shown in Figure 2, the discrepancy in the B4 fraction, N_4, between B NMR and XPS is not negligible particularly in higher K-family glasses; at small R regions, XPS gives smaller N_4 values than B NMR, suggesting that XPS also overestimates the NBO amount in these regions. At high R regions, however, XPS seems to underestimate the NBO amount. In these glasses, BO_3 units are abundant and it is therefore supposed that in XPS the amount of NBO in BO_3 units is underestimated due to the electronic delocalisation through B3–O bonds and the resultant decrease in electronic population of the NBO in the BO_3 units.

For interpreting the experimental inconsistencies correctly, theoretical approaches, such as computational modelling and molecular orbital calculation, might be indispensable. Furthermore, the whole set of measurements, including boron and silicon NMR and XPS, should be performed on the same specimens. After collecting the full information, it should be possible to propose a new universal model for the alkali distribution in borosilicate glasses.

Conclusions

Alkali distribution models were reexamined for the sodium borosilicate glasses ($RNa_2O.B_2O_3.KSiO_2$) by comparing the NBO fraction between experiments and the predictions. The NBO fractions were evaluated from O1s XPS signal and the fraction of fourfold boron, N_4 determined from ^{11}B NMR, and the amount of NBO in SiO_4 units was also estimated from the Q_n distribution determined from ^{29}Si MAS-NMR. The difference in the NBO fractions derived from the experiments was too small to choose the best model for alkali distribution.

The amounts of Na_2O consumed for the formation of BO_4 units and NBOs in SiO_4 units, R_{B4} and R_{Si} were evaluated from ^{11}B NMR and ^{29}Si MAS-NMR, respectively. The relative distribution R_{B4}/R showed a monotonic decrease with increasing R. The alkali distribution to the silicate network R_{Si}/R, however, showed a complicated change against R; in the small R region, the alkali distribution R_{Si}/R increased continuously until R reached the critical content R_{C1}, and at $R_{C1}<R<R_{C2}$, R_{Si}/R was almost constant. In the higher R region at $R_{C2}<R$, R_{Si}/R turned into decreasing. The residual Na_2O R_{B3} served the NBO formation in BO_3 units only in the region at $R_{C1}<R$.

The discrepancy was found in N_4 obtained from ^{11}B NMR and XPS; in XPS, the NBO amount seemed to be overestimated at small R region and underestimated at high R region. The overestimation of NBO amount in the small R region was also recognised in ^{29}Si MAS-NMR. It was supposed that part of the BOs in the B4–O–Si bonds had been originally NBOs in SiO_4 units and they possessed much higher electronic density than the other BOs. It was also supposed that NBOs in BO_3 units carried lower electronic densities than NBOs in SiO_4 units, resulting in the underestimation of the NBO amount in the high R region. A universal alkali distribution model would be constructed by the correct interpretation of these experimental findings.

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