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Study of Al_2O_3 effect on structural change and phase separation in Na_2O-B_2O_3-SiO_2 glass by NMR

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The effect of Al_2O_3 on the structure change and the phase separation in Na_2O-B_2O_3-SiO_2 glass was investigated using ^{11}B nuclear magnetic resonance (NMR), ^{29}Si MAS NMR, and ^{27}Al MAS NMR together with infrared absorption spectroscopy and field emission scanning electron microscopy (FE-SEM). The results show that the structure change from the introduction of Al_2O_3 contributes greatly to the inhibition of phase separation. First, the introduction of Al_2O_3 imparts an ionic character to the boron-oxygen network, resulting in the formation of B-O-Al-O-Si bonds and thus increases the compatibility of the silicon network with the boron-oxygen network. Second, the addition of Al_2O_3 causes the sodium ion to transfer from the boron-oxygen network to AlO_4 tetradedra, changing a number of four-coordinated borons into three-coordinated borons. As the bond energy of the four-coordinated boron is weaker than that of the three-coordinated boron, the -B-O-Si- bond with the four-coordinated boron in Na_2O-B_2O_3-SiO_2 glasses is easily broken and results in severe phase separation during heat treatment. However, the -B-O-Al- bond with the three-coordinated boron formed in Na_2O-B_2O_3-SiO_2-Al_2O_3 glasses is difficult to be broken due to the high bond energy. In addition, the silicon network in Na_2O-B_2O_3-SiO_2-Al_2O_3 glasses is also strengthened by the addition of Al_2O_3, which prevents [BO] groups from further aggregation. As a result, the tendency of the glass towards phase separation is greatly suppressed in the Na_2O-B_2O_3-SiO_2-Al_2O_3 system.

1. Introduction

Sodium borosilicate is the most typical glasses exhibiting phase separation and the most typical source materials for porous glasses, which are the promising materials for separation membrane, enzyme and catalyst support, photonics materials etc [1–7]. The control of the phase separation is the key step for obtaining such advanced porous materials. Aluminium oxide is an important additive to control the degree of the phase separation in sodium borosilicate glass [8, 9]. It was found that, by the addition of small amount of Al_2O_3, usually less than 3% Al_2O_3 [10], the tendency to phase separation is strongly suppressed in sodium borosilicate glass. However, this effect has not so far been unambiguously explained. Especially, few papers have dealt with the relationship between the glass structure and the phase separation systematically in Na_2O-B_2O_3-SiO_2 system glasses with small amounts of Al_2O_3 additions. From the point of view in materials design, it is very important to clarify the above relationship. For example, as phase separation is the key step for preparing porous glass, the composition and pore characteristics of the porous glass can be controlled precisely by the clarification of the relationship.

Nuclear magnetic resonance (NMR) spectroscopy has been an important tool in characterizing glass structure, providing intricate detail about the local environments presented in the glassy state [11]. Bray *et al.* studied extensively the structure of Na_2O-B_2O_3-Al_2O_3 glasses [12], K_2O-B_2O_3-Al_2O_3 glasses [13], and CaO-B_2O_3-Al_2O_3 glasses [14] by broad line nuclear magnetic resonance (NMR). More recently, W. Muller-Warmuth and H. Eckert conducted detailed quantitative structural investigations on the Na_2O-B_2O_3-Al_2O_3 system glasses by high-resolution ^{11}B, ^{23}Na and ^{27}Al NMR [15, 16]. These studies have contributed

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greatly to the development of the structural models in Na_2O-B_2O-Al_2O_3 glasses, which suggested that the boron coordination varied with the concentration of Al_2O_3. Binary Al_2O_3-SiO_2 glasses were also studied by Risbud *et al.* using ^{27}Al and ^{29}Si MAS NMR [17–25]. These glasses, made from 15–50 wt% Al_2O_3, showed that the non-bridging oxygen which was connected to Si was also affected by Al_2O_3. The structure of Na_2O-B_2O_3-SiO_2-Al_2O_3 glasses is more complicated than that of Al_2O_3-SiO_2 glasses or Na_2O-B_2O_3-Al_2O_3 glasses. However, the previous NMR measurement by W. Muller-Warmuth on glasses having the composition $(40 - x)Na_2O$-xAl_2O_3-$30B_2O_3$-$30SiO_2$, where x ranges between 0 and 25 mol%, showed both the number of nonbridging oxygens in silicate network and the number of BO_4 units have also close relation with the Al_2O_3 content [26].

In this paper, the authors investigate the structure change resulting from the addition of less than 3 mol% Al_2O_3 in a typical Na2O-B2O3-SiO2 glass which is used for preparation of porous materials, and especially, the effect on phase separation.

2. Experimental

2.1. Sample preparation

A typical glass with the composition of $9.4Na_2O$-$25.4B_2O_3$-$65.2SiO_2$ (mol%), which can exhibit spinodal phase separation by heat treatment, was used in this investigation. Sodium borosilicate glasses with the addition of 0–3 mol% were prepared from reagent grade sodium carbonate, boric acid, silica and $Al(OH)_3$. First, reagent-grade chemicals were thoroughly mixed. Then the mixtures were placed in a platinum crucible and fused at 1400°C in an electric furnace for 60 minutes. The melts were poured into carbon molds. The glasses were transparent and showed no sign of devitrification when checked by X-ray diffraction. The heat-treatment was carried out at 600°C for 72 h for the development of phase separation.

2.2. NMR measurements

(1) ^{11}B NMR measurement: The 11B NMR experiments were performed with a Chemagnetics CMX-200 operating at 64.19 MHz by pulse method. The spectra were obtained by Fourier transforming free-induction decay. The length of 90° pulse was set to 4.5 μs by using H_3BO_3 solution. For the measurement, we used a pulse as short as 1 μs to avoid undesired quadrupole effect [26]. Typically, 64 scans were used to obtain the spectra. As shown in Fig. 1, the spectrum S_3 and S_4 are from threefold- and fourfold-coordinated boron respectively.

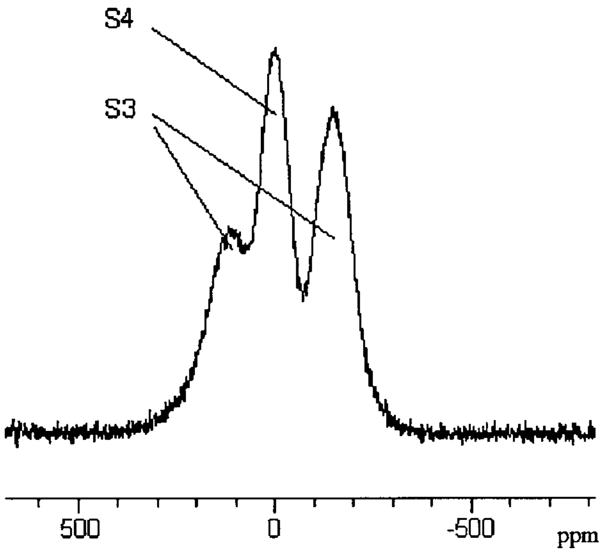

Figure 1 Pulse NMR spectrum of Na_2O-B_2O_3 sample where absorption curve corresponding to the resonance from threefold- and fourfold-coordinated boron respectively.

The pulse-FT NMR method employed in recent NMR spectrometer is usually more convenient than continuous wave method which had been used until 1970's. However, there is a drawback in this method. The acquisition of the signal is started immediately after the strong RF pulse, which is in the range of hundreds of watts. Since the receiver is designed to detect signals in the nanowatt range, it takes some time for the receiver to recover from the pulse. During this period, so called dead time, some portion of the signal is lost depending on the length of the signal in time domain. In this case, the loss of the signal from B in BO_3 is larger than that in BO_4. This causes an error in quantitative analysis from the area of each spectrum (Fig. 1). To calibrate the error, we measured a series of xNa_2O-$(1 - x)B_2O_3$ glasses, where N_4 is well known to be $x/(1 - x)$ [27], and determined the calibration factor. We also measured Li_2O- B_2O_3 glasses and some sodium borate crystals, and confirmed that this calibration factor can be used in a wide compositional range.

(2) ^{29}Si Magic Angle Spinning (MAS) NMR measurement: FT-NMR techniques in conjunction with MAS were used to obtain ^{29}Si spectra. ^{29}Si MAS NMR spectra were collected under 4.7 T with 39.789 MHz. A pulse width of 3 μs and dead time 20 μs were used. Spinning rate was 3000 Hz and the spectrum was accumulated 3200 times.

(3) ^{27}Al MAS NMR measurement: ^{27}Al MAS spectra were measured with Chemagnetics 200 spectrometer operating at 52.18 MHz. The pulse length used was 1 μ second. 300 scans were accumulated with 3 seconds of the period time between the end of the data acquisition and the start of next pulse timing sequence.

2.3. Infrared absorption spectra

Infrared-absorption spectra were measured using FT-IR-8700. The spectra of the glasses in the range of 400–4000 cm^{-1} were taken by a double-beam recording spectrophotometer.

2.4. SEM measurement

Field emission scanning electron microscope (FE-SEM), model S-5000 by Hitachi Ltd., was used to examine the microstructure of the cross-section of the heat-treated samples with the different amount of Al_2O_3 addition. The cross-section of the samples was etched by 3% HF solution before it was coated with a thin layer of carbon.

3. Results

3.1. The dependence of the fraction of four-coordinated boron (N_4) on the Al_2O_3 content

The ^{11}B NMR spectra of the samples with 0, 0.5, 1, 2, and 3 mol% Al_2O_3 are shown in Fig. 2. It can be seen that the peaks corresponding to three-coordinated boron increase with the amount of Al_2O_3. This suggests that the fraction of four-coordinated boron in the samples decreases with the addition of Al_2O_3. The results of a quantitative calculation by fitting the ^{11}B NMR spectrum using the computer software of NMR data processing program is shown in Fig. 3. The fraction of four-coordinated boron (N_4) is 29% for the 9.4Na_2O-25.4B_2O_3-65.2SiO_2 glass without Al_2O_3. It decreases to 21% for the 9.4Na_2O-25.4B_2O_3-65.2SiO_2 glass with 3% Al_2O_3. The curve of N_4 versus Al_2O_3 also shows that the N_4 decreases with increasing Al_2O_3 content.

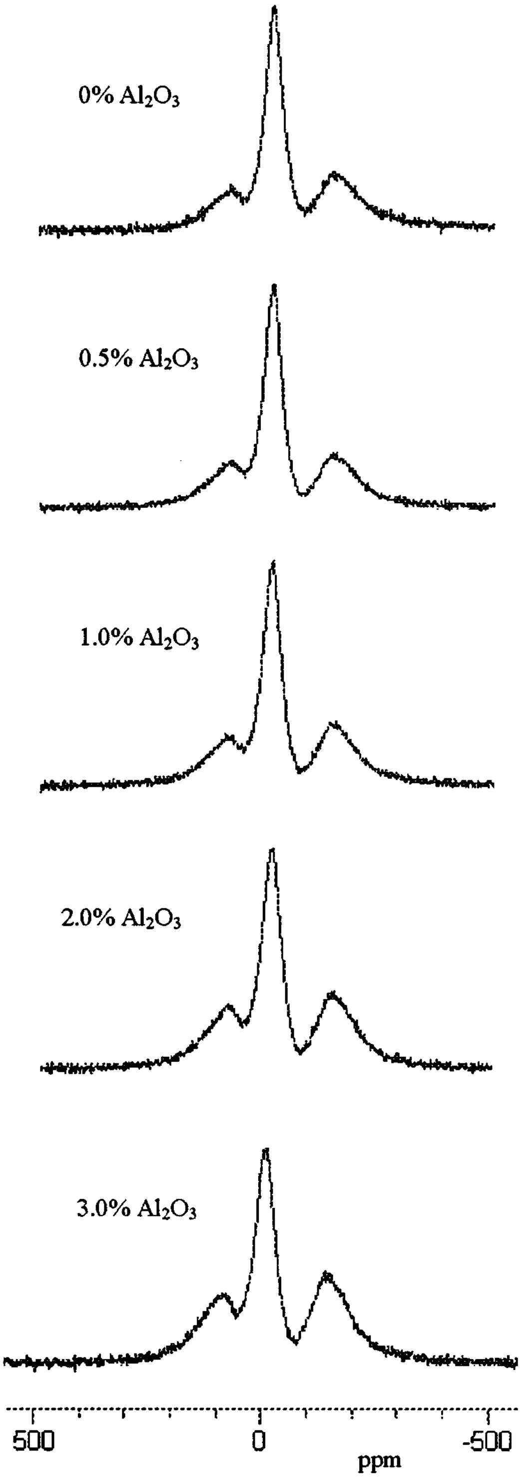

Figure 2 ^{11}B NMR spectrum of the Na_2O-B_2O_3-Si_2O glasses with the addition of Al_2O_3.

3.2. ^{29}Si NMR spectra

Fig. 4 shows ^{29}Si MAS NMR spectra of the Na_2O-B_2O_3-Si_2O glasses without Al_2O_3 and with 3% Al_2O_3, respectively. ^{29}Si MAS NMR is capable of discriminating by characteristic chemical shifts between the five different SiO_4 tetrahedra connected with 0–4 other such tetrahedra, i.e. Q^0, Q^1, Q^2, Q^3, and Q^4 (the superscript gives the number, *m*, of SiOSi linkages of the $Si(OSi)_m(O\text{-})_{4-m}$ structural units Q^m). The usual values for the mean chemical shifts used to fit the spectra of glasses are −107 ppm (Q^4), −92 ppm (Q^3), −82 ppm (Q^2), −69 ppm (Q^1), and −63 ppm (Q^0) [28]. Though it is apparent that, by Fig. 4, no Q^0, Q^1, and Q^2

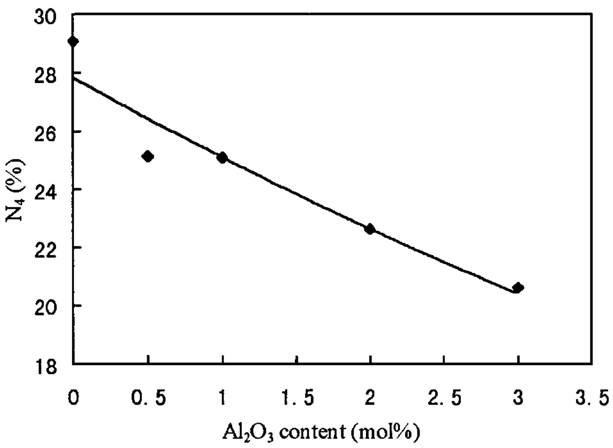

Figure 3 Relation between Al_2O_3 content and the fraction of fourfold coordinated boron (N_4) in Na_2O-B_2O_3-Si_2O glass by ^{11}B NMR measurement.

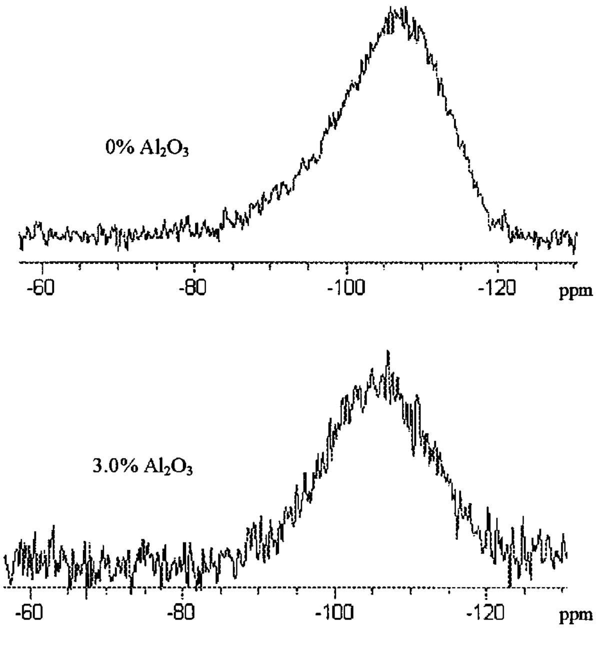

Figure 4 ^{29}Si MAS NMR spectrum of the Na_2O-B_2O_3-SiO_2 glasses without Al_2O_3 and with 3% Al_2O_3.

units exist in the samples, the ^{29}Si MAS NMR spectrum of the sample without Al_2O_3 shows asymmetry within -107––92 ppm, which suggests a spectrum resulting from the overlap of Q^3 and Q^4. This will be confirmed later in the discussion section. However, the ^{29}Si MAS NMR spectrum of the sample with 3% Al_2O_3 shows only Q^4 units.

3.3. ^{27}Al NMR spectra

Aluminium usually occurs in four-fold and/or six-fold coordination as a intermediate in glass [8]. AlO_6 octahedra gives resonance at a position of ∼0 ppm whereas AlO_4 tetrahedra gives resonance in the region 50–60 ppm. In this work, ^{27}Al NMR spectra show a single sharp peak at 50 ppm (Fig. 5), which clearly indicates that Al forms AlO_4 tetrahedra in the glass.

3.4. Infrared absorption spectra

The infrared absorption spectrum of the Na_2O-B_2O_3-SiO_2 glass without Al_2O_3 and that of the same glass with 2% and 3% Al_2O_3 are shown in Fig. 6, respectively. The absorption bands of Si-O near 800 cm^{-1} and O-Si-O near 1060 cm^{-1} broaden with Al_2O_3. Besides the absorption bands of the samples with Al_2O_3 additive exhibit larger half-bandwidths, the absorption bands of the samples with Al_2O_3 additive also have lower frequencies. It can be seen that the absorption of 2% Al_2O_3 sample at 1060 cm^{-1} shifts towards lower frequencies by 10–15 cm^{-1} compared with that of the Na_2O-B_2O_3-SiO_2 glass without Al_2O_3.

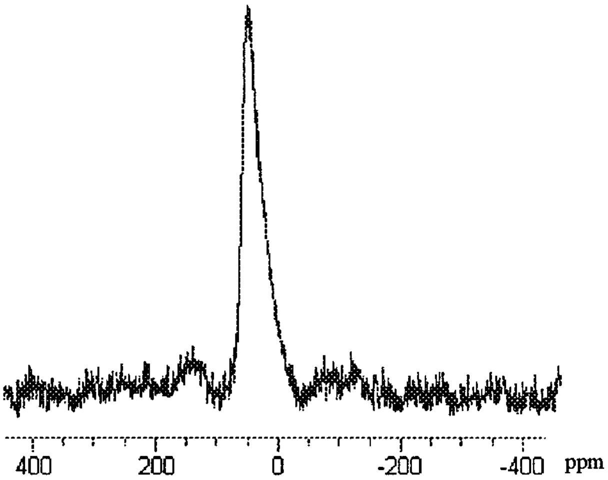

Figure 5 ^{2}7Al MAS NMR spectrum of the Na_2O-B_2O_3-Si_2O glasses with 3% Al_2O_3.

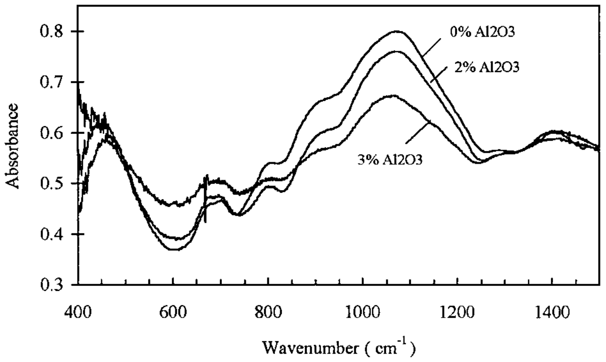

Figure 6 IR spectra of $9.4Na_2O$-$25.4B_2O_3$-$65.2SiO_2$ glass without Al_2O_3 additive and with Al_2O_3 additive.

TABLE I The color of the samples after heat treatment

Sample	Heat treatment	Sample color
0% Al_2O_3	600°C, 72 h	White with blue
0.5% Al_2O_3		blue
1.0% Al_2O_3		Weak blue
2.0% Al_2O_3		Very weak blue
3.0% Al_2O_3		transparent

3.5. SEM observation

After a heat treatment at 600°C for 72 h, it is easy to observe that a color change in the sample. This is caused by Rayleigh scattering due to the different refractive index of the immiscible phases when the spinodal phase separation occurs. With the addition of Al_2O_3, the white and the blue colors fade, as shown in Table I. The SEM micrographs of the samples without Al_2O_3 and with 2% and 3% Al_2O_3 after heat treated are showed in Fig. 7. In Fig. 7, the pore area corresponds to boron-rich phase which is leached out by 3% HF solution. The remained network skeleton is Si-rich phase. From Fig. 7a, it can be seen that the phase separation develops in the Na_2O-B_2O_3-SiO_2 glass without Al_2O_3. In Fig. 7c, SEM photograph exhibits that the sample with 3% Al_2O_3 have little boron-rich phase and the tendency of the phase separation decreases greatly.

4. Discussion

4.1. Al_2O_3 effect on the structural change in Na_2O-B_2O_3-SiO_2 glass

By Figs 2 and 3, it can be seen that the fraction of fourfold coordinated boron (N_4) decreases with the addition of Al_2O_3. Alumina is network-forming oxide for glasses. In the present research it is confirmed by Fig. 5 that aluminium is distributed among the sites of one-charged tetrahedral units in $9.4Na_2O$-$25.4B_2O_3$-$64.2SiO_2$ glasses. Hence, with the addition of Al_2O_3, $AlO_{4/2}^-$ tetrahedra is formed in Na_2O-B_2O_3-SiO_2-Al_2O_3 system glasses. To keep the equilibrium of electric field, it is assumed that the formation of charged $AlO_{4/2}^-$ units is at the expense of four-coordinated boron, resulting in the decrease of N_4 in Na_2O-B_2O_3-SiO_2-Al_2O_3, as illustrated in Fig. 8.

However, the amount of Na^+ cation transferred to $AlO_{4/2}^-$ is still not enough to keep the equilibrium of electric field. In $9.4Na_2O$-25.4_2O_3-$65.2SiO_2$ glass with 3 mol % Al_2O_3, i.e. in $9.4Na_2O$-$25.4B_2O_3$-65.2SiO2-$3Al_2O_3$ glass, as 6 mol units of $AlO_{4/2}^-$ are formed, it needs 6 mol cations to keep the equilibrium of electric field. By Fig. 3, the fraction of the four-coordinated boron (N_4) is 29% and 21% in $9.4Na_2O$-$25.4B_2O_3$-$65.2SiO_2$ glass without Al_2O_3 and with 3% Al_2O_3, respectively. The amount of destroyed BO_4 units by the addition of 3% Al_2O_3 is:

$$0.29 \times 25.4 \times 2 - 0.21 \times 25.4 \times 2 = 4\,(\text{mol})$$

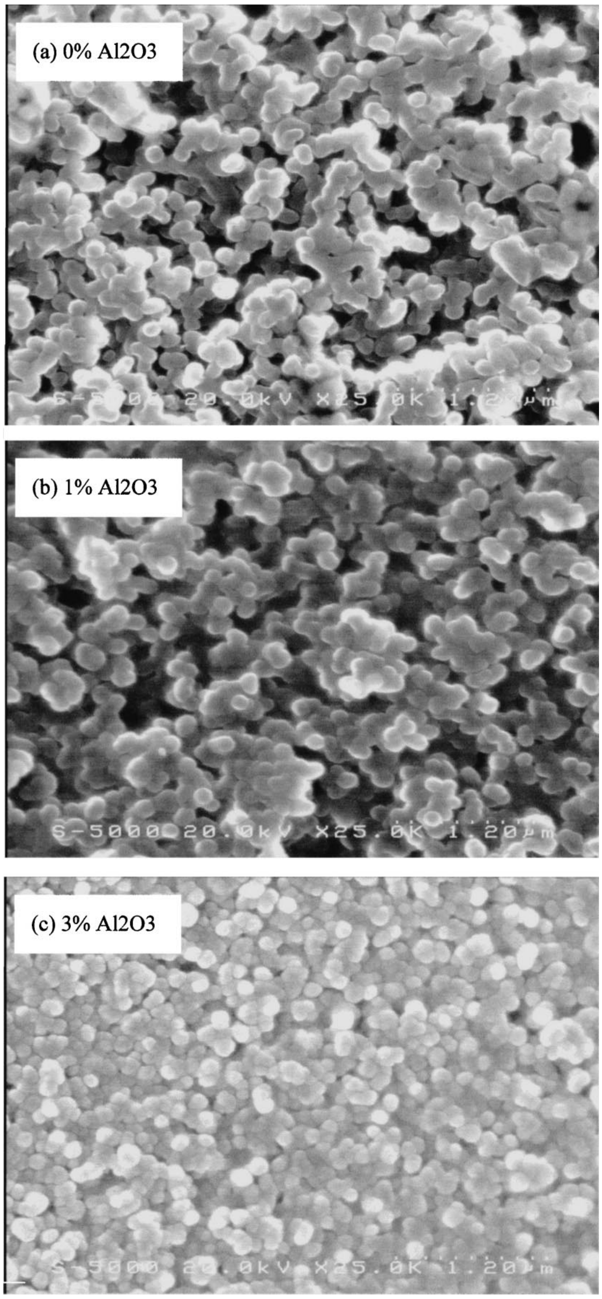

Figure 7 SEM micrographs of the samples after heat treated at 600°C for 72 h. (a) 0% Al_2O_3, (b) 1% Al_2O_3, (c) 3% Al_2O_3.

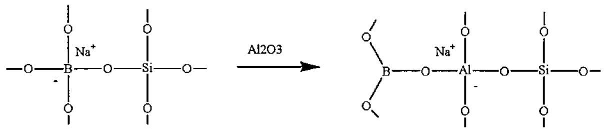

Figure 8 Al_2O_3 effect on the structure change of boron network.

Hence, there should be only 4 mol Na^+, which was distributed among the sites of BO_4 group, is transferred to the sites of $AlO_{4/2}^-$ after addition of 3% Al_2O_3. So, we assume that the structure of Si network is also affected by the addition of Al_2O_3 and it also contributes to keep the equilibrium of electric field.

By Fig. 4, it can be seen that the ^{29}Si spectra of 0% Al_2O_3 sample is asymmetrical around −92 ppm, which suggests that besides Q^4 group, there also exists Q^3 group in Si network. Fig. 9 is the line fit of ^{29}Si spectra of 0% Al_2O_3 sample, which clearly shows that there exists about 4% Q^3 against total Si network.

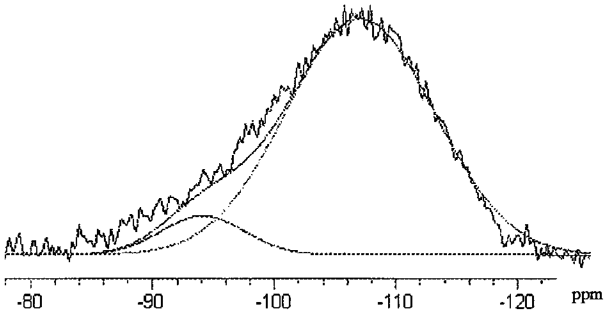

Figure 9 Line fit showing besides uncharged $SiO_{4/2}$ group (Q^4, containing no NBOs), there exits a little amount of the singly charged SiO5/2- group (Q^3, containing one NBO) in Na_2O-B_2O_3-SiO_2 glass.

The formation of Q^3 group in Si network is caused by a small amount of Na^+ that is distributed among the Si network, which destroys Q^4 groups. This can be confirmed by the comparison of the ^{11}B spectra of $9.4Na_2O$-$25.4B_2O_3$ glass with that of $9.4Na_2O$-$25.4B_2O_3$-$65.2SiO_2$ glass, as shown in Fig. 10. The peak which corresponds to the four-coordinated boron in $9.4Na_2O$-$25.4B_2O_3$-$65.2SiO_2$ glass is narrowed as compared with that of $9.4Na_2O$-$25.4B_2O_3$ glass, which suggests a decrease in N_4. Quantitative calculation by fitting the ^{11}B NMR spectrum using the computer software of NMR data processing program exhibits that $9.4Na_2O$-$25.4B_2O_3$ glass has 37% four- coordinated boron (Fig. 11). However, N_4 decreases to 29% in $9.4Na_2O$-$25.4B_2O_3$-$65.2SiO_2$ glass. For boron network, as the addition of each sodium oxide can lead to the formation of one (BO_4)-tetrahedra, N_4 value is therefore considered to correspond to the amount of sodium ions which are distributed among the boron network. Hence, the decrease of N_4 in $9.4Na_2O$-$25.4B_2O_3$-$65.2SiO_2$ also means that the Na^+ which is distributed in boron network is removed. It is no doubt that these Na^+ ions were transferred into the Si network, resulting in the formation of Q^3 groups.

However, Q^3 group disappeared after the addition of 3% Al_2O_3 (Fig. 4). This confirms that Q^3 groups change to Q^4 group by the connection of AlO units, as described by structural model in Fig. 12. Thus, we can calculate the amount of sodium ions which move to $AlO_{4/2}$-tetrahedra by the following theoretical formula:

$$\begin{aligned} N_{Al} &= N_B + N_Q \\ &= (0.29 \times 25.4 \times 2 - 0.21 \times 25.4 \times 2) \\ &\quad + 65.2 \times 0.04 \\ &= 6.6\,(\text{mol}) \end{aligned}$$

where N_{Al} denotes the amount of sodium ions which move to $AlO_{4/2}$-tetrahedra, N_B denotes contribution by destroying of four-coordinated boron, and N_Q denotes contribution by formation of Q^4. The calculated result nearly approaches the theoretical value by the introduction of 3% Al_2O_3, i.e. 6 mol ions of sodium should move to $AlO_{4/2}$-tetrahedra by the introduction of 3% Al_2O_3. The result further support our supposal.

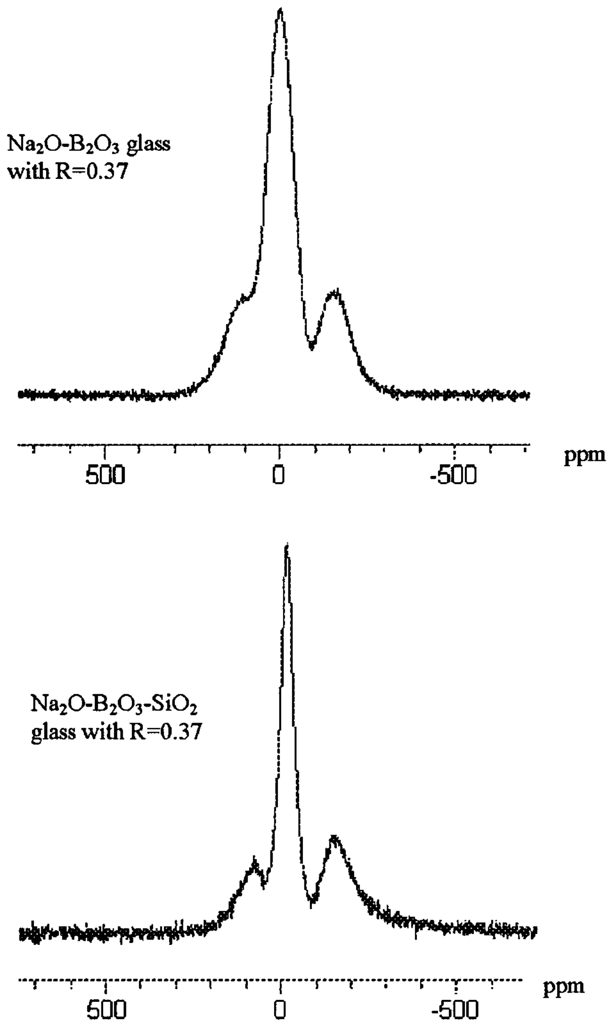

Figure 10 ^{11}B NMR spectrum showing the peak corresponding to four-coordinated boron narrowed in Na_2O-B_2O_3-SiO_2 glass.

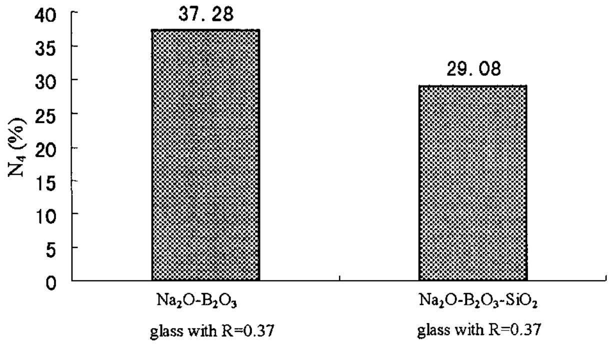

Figure 11 The fraction of the four-coordinated boron (N_4) decreased in Na_2O-B_2O_3-SiO_2 glass.

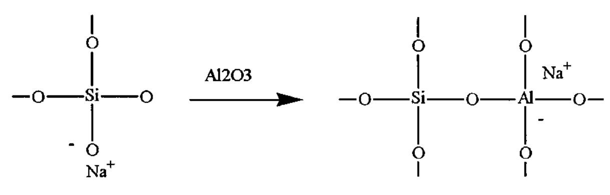

Figure 12 Al_2O_3 effect on the structure change of silica network.

4.2. Al_2O_3 effect on the phase separation

Al_2O_3 effect on the inhibition of the phase separation is apparent. By Fig. 7a, the spinodal separation into Si-rich phase and boron-rich phase is strongly developed in Na_2O-B_2O_3-SiO_2 glass without the addition of Al_2O_3. This spinodal phase separation is greatly inhibited after 3% Al_2O_3 was introduced, as Fig. 7c shows the pore size, which is corresponding to the second phase leached by HF solution, decreases dramatically. Table I also provides the fact of Al_2O_3 effect on phase separation. When homogeneous glass separated strongly into two immiscible phase for 0% Al_2O_3 sample, light is mostly reflected due to the large size of separated phase, resulting in opaque white color based on Rayleigh scattering. With the addition of Al_2O_3, the phase separation decreases to a smaller degree. As the size of the separated phase is very small, most light is only refracted through the sample. Thus we observe the blue color for 0.5% Al_2O_3 1.0% Al_2O_3, and 2.0% Al_2O_3 samples.

The mechanism of Al_2O_3 effect on the inhibition of the phase separation has close relation with the structure change in Na_2O-B_2O_3-SiO_2-Al_2O_3 glasses. First, the introduction of Al_2O_3 imports an ionic character to boron-oxygen network, resulting in the formation of B-O-Al-O-Si bond and thus increasing the compatibility of silicon network with boron-oxygen network. Second, as the sodium ion transfers from boron-oxygen network to AlO_4 tetradedra, a number of four-coordinated boron changes into three-coordinated boron. In Na_2O-B_2O_3-SiO_2 glass, the phase separation is supposed to be caused by the competition for the oxygen anions between Si^{4+} ions and B^{3+} ions in B-O-Si bond [2]. The bond energy of the four-coordinated boron, which is 89 kcal/mol, is weaker than that of the three-coordinated boron, which is 119 kcal/mol [29]. Thus, the -B-O-Si- bond with four-coordinated boron in Na_2O-B_2O_3-SiO_2 glasses is easily broken and result in severe phase separation during heat treatment. However, the –B-O-Al- bond with three-coordinated boron formed in Na_2O-B_2O_3-SiO_2-Al_2O_3 glasses is difficult to be broken due to the high bond energy. As a result, the tendency of the glass towards phase separation is greatly suppressed in Na_2O-B_2O_3-SiO_2-Al_2O_3 system. Fig. 13 illustrated the dynamic mechanism of Al_2O_3 for increasing compatibility between Si network and boron network.

From Fig. 6, it can also be seen that the Si-O band at 1060 cm^{-1}, and O-Si-O band at 800 cm^{-1} are all

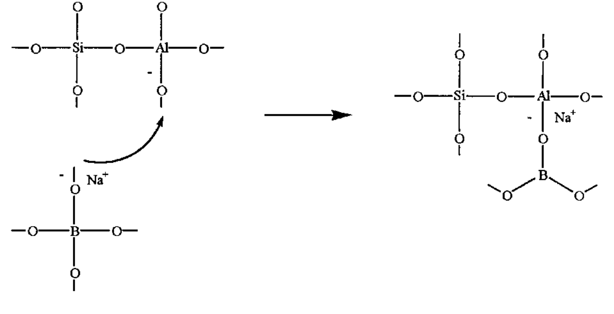

Figure 13 Illustration suggesting a mechanism for Al_2O_3 increasing the compatibility between Si network and boron network.

broadened with the addition of Al_2O_3. The broadening of the lines in this region is due to a statistical distribution of structural parameters such as bond angles [26]. It is no doubt that Si atoms with one boron next-nearest neighbor or one Al next-nearest neighbor via oxygen have wider distribution of bond angles. On the other hand, the distribution of the bond angles of Si atoms mostly connected to other Si via oxygen is narrow. It is indicated by Fig. 6 that Si atoms in the samples with Al_2O_3 are connected with one boron next-nearest neighbor or one Al next-nearest neighbor via oxygen, thus the Si-O band is broadened. For the sample without Al_2O_3, it is possible that the phase separation in very small size scale actually occurs even during cooling from melt in Na_2O-B_2O_3-SiO_2 glass. As some of the Si-O-B bond are broken after phase separation, Si atoms are mostly connected to other Si via oxygen, resulting in sharpening of the Si-O band. This further supports that the compatibility between boron network and Si network increases by the addition of Al_2O_3.

In addition, another possible mechanism of Al_2O_3 effect on the inhibition of the phase separation is that SiO network is strengthened. During heat treatment, BO groups tend to pass through the SiO network to aggregate. This is relatively easy in Na_2O-B_2O_3-SiO_2 glass without Al_2O_3 as Q^3 with one non-bridging oxide exists, which provide a path for BO group moving. The Na_2O-B_2O_3-SiO_2 glass with Q^3 can be thought as a Si-network with some defects. However, the ^{29}Si NMR spectra (Fig. 4) shows there exists no Q^3 for 3% Al_2O_3 sample. The defects of the Si-network in Na_2O-B_2O_3-SiO_2 are repaired by Al_2O_3 (see Fig. 12). So, it is difficult for BO group moving through the Si-network to aggregate, resulting in the difficulty in phase separation.

5. Conclusions

With the addition of Al_2O_3, ^{11}B NMR spectrum showed that the fraction of the fourfold-coordinated boron decreased in Na_2O-B_2O_3-SiO_2 glass. This is caused by the formation of one-charged tetrahedral $AlO_{4/2}$-units at the expense of BO_4 group. ^{29}Si MAS NMR spectrum showed that the Si network in Na_2O-B_2O_3-SiO_2 glass without the addition of Al_2O_3 is composed by Q^4 units and Q^3 units. However, after introduction of 3% Al_2O_3, Si network is mainly composed of Q^4 units.

The introduction of Al_2O_3 firstly imparts an ionic character to the network with the boron-oxygen network, resulting in the formation of B-O-Al-Si bond and thus increasing the compatibility of the network with the boron-oxygen. Second, as the sodium ion transfers from boron-oxygen network to Al_2O_3 tetradedra, the four-coordinated boron changes into three-coordinated boron with higher bond energy. The -B-O-Al- bond with the three-coordinated boron formed in Na_2O-B_2O_3-SiO_2-Al_2O_3 glasses is more difficult to be broken than the –B-O-Si bond with four coordinated boron in Na_2O-B_2O_3-SiO_2 glass during heat treatment. As a result, the tendency of the glass towards phase separation is greatly suppressed in Na_2O-B_2O_3-SiO_2-Al_2O_3 system. In addition, the silicon network in Na_2O-B_2O_3-SiO_2-Al_2O_3 glasses is also strengthened by the addition of Al_2O_3, which prevents [BO] groups from further aggregation and phase separation.

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