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Study of kinetics of the phase separation in sodium borate glasses

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The kinetics of the phase separation in 15Na_2O-85B_2O_3 binary glasses was investigated using ^{11}B nuclear-magnetic-resonance (NMR) spectra, X-ray diffraction (XRD) and scanning electron microscopy (SEM) observation. It was found that the equilibrium of the phase separation took long time due to the growth of a boron-rich phase and the composition fluctuation in Na-rich phase. Although the XRD results showed that the development of the boron-rich phase was through nucleation and growth, the NMR spectra indicated that the sodium-rich phase always occurred as amorphous glasses with fluctuation in composition during the phase separation. This may result from that the over-coordination of oxygen atoms in the sodium-rich phase, which renders difficulties in the crystallization of the sodium-rich phase with less than 75 mol% sodium oxides. It was found that, at 500°C, the 15Na_2O-85B_2O_3 glasses was finally separated into $Na_2O{\cdot}9B_2O_3$ and $3Na_2O{\cdot}B_2O_3$ rather than those being proposed by the conventional phase diagram. © *2000 Kluwer Academic Publishers*

1. Introduction

Sodium borosilicate glass is one of the phase separation glasses and the most typical source materials for porous glasses [1–4], which are the promising materials for separation membrane, enzyme and catalyst support, photonics etc. For the homogeneous sodium borosilicate glass, it was found that sodium cation preferentially associated itself with the borate network [5–7]. During heat treatment, the sodium metal ions may migrate to those groups in which boron has latent conditions for separation. This migration of the sodium cation results in a local accumulation of cations and subsequent pre-separation in Na_2O-B_2O_3 system, which would lead to the final separation to boron-rich phase and SiO_2-rich phase in sodium borosilicate ternary glass [5]. From the point of view in materials design, it is very important to clarify the phase separation process in binary Na_2O-B_2O_3 system. For example, as phase separation is the key step for preparing porous glass, the composition and pore characteristics of the porous glass are controlled precisely by a clarification of the kinetics of the phase separation in sodium borate glasses.

The sodium borosilicate glass with a ratio of $Na_2O : Ba_2O_3 \cong 15 : 85$ exhibits the strongest tendency toward phase separation [5]. Concerning the Na_2O-B_2O_3 binary system, it is usually thought that the decomposition of the 15Na_2O-85B_2O_3 glass leads to products close to the original composition during heat treatment. The phase diagram of the binary Na_2O-B_2O_3 system shows that the phase equilibrium for 15Na_2O-85B_2O_3 remains between $Na_2O{\cdot}9B_2O_3$ and $Na_2O{\cdot}4B_2O_3$ [8, 9]. However, these data of the phase equilibrium of the binary Na_2O-B_2O_3 system were mainly obtained at temperatures higher than 600°C. The temperature of the phase separation for preparation of porous glasses is relatively lower. In addition, the previous investigation on the phase equilibrium relationship was conducted using only the X-ray diffraction technique. The evidence based on this experiment is still ambiguous to some extent, since the difference of the X-ray diffraction peaks obtained from various sodium borate compounds is very small. In the present paper, we explore the dynamic process of the phase separation in Na_2O-B_2O_3 glasses by several techniques, including nuclear magnetic resonance and present new data of the phase equilibrium at 500°C. The results suggested difficulty in the crystallization of sodium-rich phase due to the over-coordination of oxygen atoms. Consequently, it actually takes long time for the Na_2O-B_2O_3 glasses to reach equilibrium during phase separation. The phase

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equilibrium in sodium borate glasses is controlled by the competition between the rates of the nucleation and crystal growth involving two immiscible phases that differ from those of the conventional phase diagram.

2. Experimental

2.1. Sample preparation

The sodium borate glasses used in this investigation were prepared from reagent grade sodium carbonate and boric acid. First, reagent grade sodium carbonate Na_2CO_3 and boric acid H_3BO_3 were thoroughly mixed together. Then the mixtures were placed in a platinum crucible and fused at 1000°C in an electric furnace for 30 minutes. The melts were poured into carbon molds. For those samples in which sodium content is larger than 33.3%, the melt was poured onto a metal plate and quickly covered with a brass block. Samples were transparent and showed no sign of devitrification when checked by X-ray diffraction techniques. The samples were immediately kept in a sealed plastic bag at humidistat to ensure they were not interfered by humidity. The glass transition temperature is about 400°C [8]. Phase separation was carried out at 400–550°C for 5–30 h using $15Na_2O$-$85B_2O_3$ glass.

2.2. NMR measurements

The ^{11}B NMR experiments were performed at 64.19 MHz. 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 the distortion of the spectra from quadrupole effects [10]. Typically, 64 scans were used to obtain the spectra. Bray *et al.* have extensively studied the structure of the homogeneous glass containing boron by NMR [11–20]. It has been shown that boron atoms exist as either threefold or fourfold coordination with network oxygen. Fig. 1 shows a typical example of the pulse ^{11}B NMR spectrum in borate glasses. The spectrum S_3' and S_4' are from threefold- and fourfold-coordinated boron respectively. In general, the difference in NMR spectra between BO_3 unit and BO_4 unit is due to structural difference between BO_3 and BO_4. The BO_3 unit employs planer structure in which the boron lies at the center of an oxygen triangle. This configuration produces the large electric field gradient vertical to the plane, and as a result the nuclear quadrupole moment of ^{11}B ($I = 3/2$) in BO_3 becomes considerably large (2.6–2.8 MHz) [21]. Due to the large quadrupole moment, the adsorption from the central transition of ^{11}B ($-1/2 \leftrightarrow 1/2$) shows a doublet pattern from the second order quadrupole interaction, as shown in Fig. 1. On the other hand, in the BO_4 unit, the boron is located at the center of an oxygen tetrahedron. The quadrupole moment becomes small because of the symmetry around ^{11}B, so that a single resonance line is observed for the ($-1/2 \leftrightarrow 1/2$) transition. These two specific ^{11}B adsorptions from BO_3 and BO_4 can easily be separated, which enables one to obtain the fraction of each species. The method has been widely used to obtain the fraction of BO_3 and BO_4 in glasses since late 1960's.

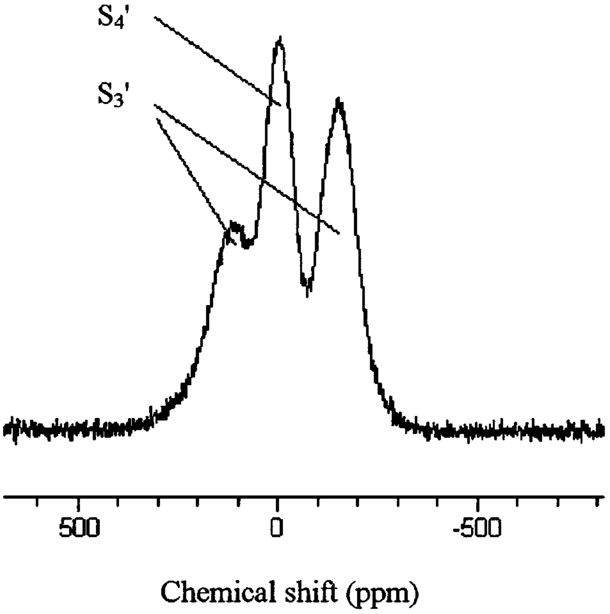

Figure 1 Pulse ^{11}B NMR spectrum of Na_2O-B_2O_3 sample where absorption curve corresponding to the resonance from threefold- and fourfold-coordinated boron respectively.

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 of 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 $x Na_2O$-$(1-x)B_2O_3$ glasses without phase separation, where x is the molar percent of Na_2O in the glasses. Since the fraction of the four-coordinated boron N_4, i.e. $S_4/(S_3+S_4)$, in the $x Na_2O$-$(1-x)B_2O_3$ glasses without phase separation is well known to be $x/(1-x)$ [11], we can determine the calibration factor a and b with response to the S_3' and S_4' from the pulse NMR measurement by using the equation

$$\frac{x}{(1-x)} = \frac{aS_4'}{(aS_4' + bS_3')} = \frac{S_4'}{\left[S_4' + \left(\frac{b}{a}\right)S_3'\right]} \tag{1}$$

where $x/(1-x)$ is the molar ratio of Na_2O vs B_2O_3 (R) in the $x Na_2O$-$(1-x)B_2O_3$ glasses, i.e.:

$$\frac{x}{(1-x)} = R \tag{2}$$

Therefore,

$$\frac{1}{R} = \left(\frac{b}{a}\right)\left(\frac{S_3'}{S_4'}\right) + 1 \tag{3}$$

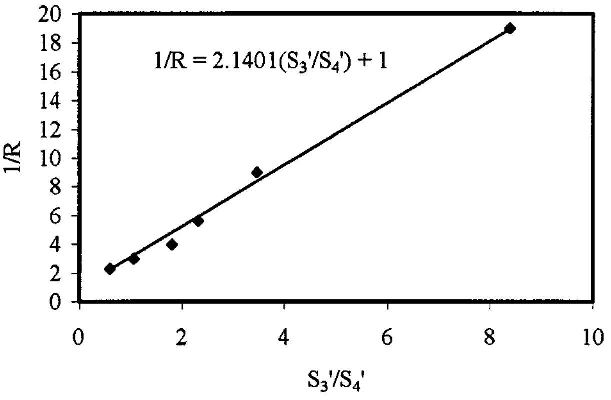

Figure 2 Linear relation between S'_3/S'_4 and $1/R$, showing calibration factor b/a for pulse ^{11}B NMR is 2.1401.

The calibration factor b/a can be therefore calculated out from the slope of $1/R \sim S'_3/S'_4$ by measuring the pulse NMR spectra of a series of xNa$_2$O-$(1-x)$B$_2$O$_3$ glasses without phase separation, as shown in Fig. 2. Thus, the real N$_4$ by calibrating the pulse NMR measurement is given by

$$N_4 = \frac{S'_4}{(S'_4 + 2.1401S'_3)} \tag{4}$$

We also measured homogeneous Li$_2$O-B$_2$O$_3$ glasses and some sodium borate crystals, and confirmed that this calibration factor can be used in a wide compositional range.

2.3. XRD and SEM measurement

X-ray diffraction (XRD) patterns were recorded with Cu K$_\alpha$ radiation at a scanning step of 0.1 in the 2θ range 5–60, under the operation condition of 40 KV–20 mA. Scanning electron microscopy (SEM) was used to examine the microstructure of the cross-section of the samples with different heat treatment times. The cross-section surfaces of the samples were washed with water before they were coated with a thin layer of gold.

3. Results

3.1. XRD

Samples with different time of heat treatment were firstly measured by X-ray diffraction technique as the color changed from transparent to opaque during heat treatment (Table I). This possibly indicated that crystallization occurred during the propagation of phase separation. As expected, XRD patterns exhibited peaks of a crystal phase (Fig. 3 and Table II). It is interesting to note that: (1) When the heat treatment time is shorter than 20 hours, the X-ray diffraction peaks coincide very well with $Na_2O{\cdot}9B_2O_3$ crystal, which indicates that the boron-rich phase of the decomposed products is $Na_2O{\cdot}9B_2O_3$. It can be deduced that the sodium-rich phase is still amorphous since only one crystallized phase was found. In addition, the intensity of the peaks increases with heat treatment time (Fig. 4), indicating that the amount of this boron-rich phase is increased in the course of the phase separation. The results suggest that, in this stage of the phase

TABLE I N$_4$ value and glass color of 15%Na$_2$O-85%B$_2$O$_3$ samples after different heat treatment condition

Heat-treated conditon		N$_4$ by NMR measurement	
Temperature (°C)	Time (hours)	(%)	Glass color
500	0	17 ± 0.85	Transparent
500	5	16 ± 0.80	Surface is opaque, inside is transparent
500	10	16 ± 0.80	Outside layer is opaque, inside layer is transparent
500	15	13 ± 0.65	Outside layer is opaque, inside layer is transparent
500	20	10 ± 0.50	Throughly opaque
500	25	11 ± 0.55	Throughly opaque
500	30	10 ± 0.50	Throughly opaque

TABLE II The composition of crystallized phases at different heat treatment condition

Heat treatment time (hours)	Crystallized phase (by XRD analysis)
0	x
5	Na$_2$O.9B$_2$O$_3$
10	Na$_2$O.9B$_2$O$_3$
15	Na$_2$O.9B$_2$O$_3$
20	a: Na$_2$O.9B$_2$O$_3$ b: unknown new crystal
25	a: Na$_2$O.9B$_2$O$_3$ b: unknown new crystal
30	a: Na$_2$O.9B$_2$O$_3$ b: unknown new crystal

x: there does not exist crystal phase in original glass.

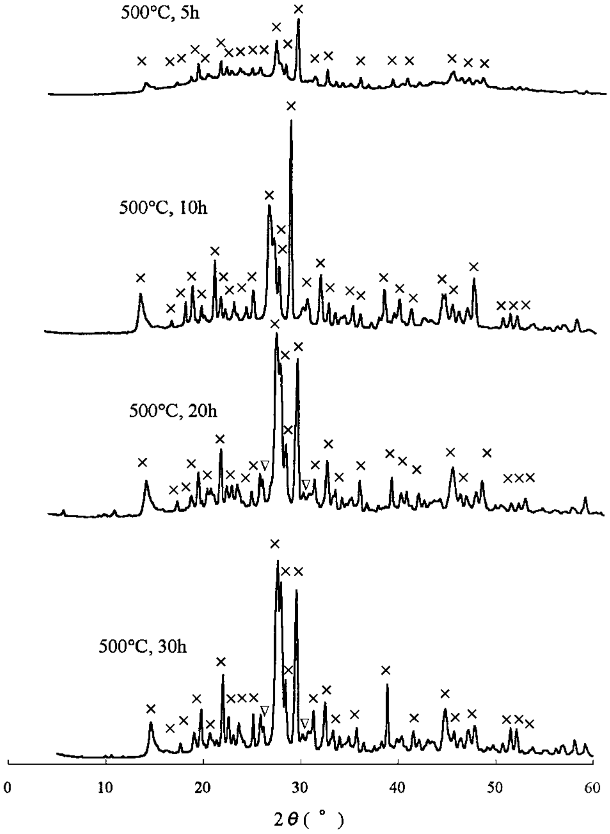

Figure 3 XRD patterns of 15Na$_2$O-85B$_2$O$_3$ glass after heat treatment; × $Na_2O \cdot 9B_2O_3$ crystal, △ New crystal.

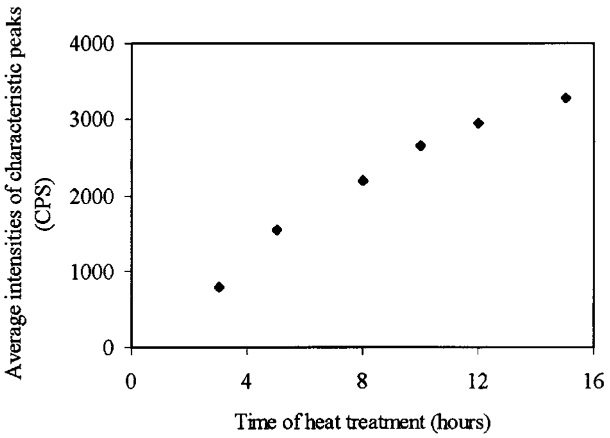

Figure 4 The dependence of the average intensities of $Na_2O{\cdot}9B_2O_3$ XRD peaks on heat treatment time.

separation, phase equilibrium is still not reached. (2) When the heat treatment time is longer than 20 h, the X-ray diffraction pattern is not changed by further heat treatment, which indicates that the phase equilibrium has been reached. Some new diffraction peaks, which could come from the sodium-rich crystal, occur beside the diffraction peaks of $Na_2O{\cdot}9B_2O_3$.

However, it is still difficult to completely distinguish the new diffraction peaks after 20 h of heat treatment only according to XRD data, as a large number of these diffraction peaks are very weak. In addition, many of the sodium borate compounds, such as $Na_2O{\cdot}4B_2O_3$, $Na_2O{\cdot}B_2O_3$, and $3Na_2O{\cdot}B_2O_3$, have similar diffraction peaks along with the new diffraction peaks. This makes it difficult to distinguish the various compounds.

3.2. Microstructure observation

The SEM photographs of the samples with different heat treatment time are shown in Fig. 5. The SEM photograph coincides well with our XRD data. It can be seen from Fig. 5 that when the heat treatment time is shorter than 20 hours, the $Na_2O{\cdot}9B_2O_3$ crystal at first grows gradually from the matrix glass. Then the residual sodium-rich glass crystallizes after 20 hours of heat treatment time. The volume fractions of the separated phases can be roughly estimated by lineal analysis by tracing and cutting phase outlines on polyester sheet and weighing both fractions [22]. The result shows that the volume fraction of the sodium-rich phase is about 5–10% after reaching equilibrium. However, this result does not agree with those being proposed by the conventional phase diagram. The phase diagram suggests that the $15Na_2O\text{-}85B_2O_3$ glass decomposes into $Na_2O{\cdot}9B_2O_3$ and $Na_2O{\cdot}4B_2O_3$, according to following reaction model [8]:

$$15Na_2O\text{-}85B_2O_3 \rightarrow 5(Na_2O{\cdot}9B_2O_3) + 10(Na_2O{\cdot}4B_2O_3) \quad (5)$$

This reaction model for the phase separation shows that the weights of the boron-rich phase and sodium-rich phases are nearly 50% respectively. Because of

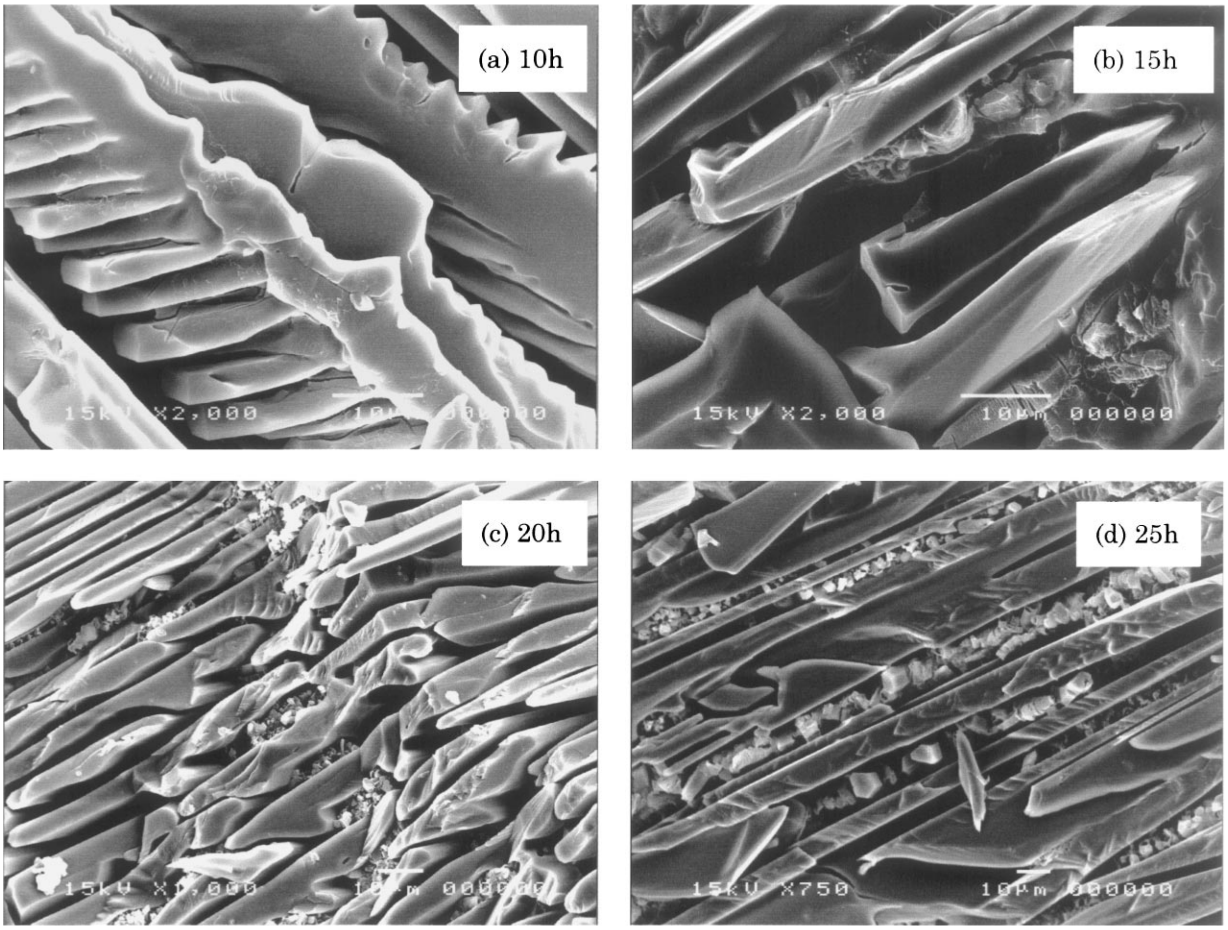

Figure 5 The SEM photographs of the samples with different heat treatment time.

the similarity in densities of the boron-rich phase and the sodium-rich phase which contain small amounts of sodium, the volume of the boron-rich phase and sodium-rich phase may also be assumed to be close to 50% respectively. Whereas, the SEM observation of the present investigation, as shown in Fig. 5, exhibits that the volume fraction of the sodium-rich phase is about 5–10% after reaching equilibrium. According to mass balance, this small amount of boron-rich phase should have much higher content of sodium oxide than $Na_2O{\cdot}4B_2O_3$ that is suggested by phase diagram. However, since the microstructure of the separated phases is anisotropic (Fig. 5), the result of the linear analysis of the SEM photograph should be very rough. The SEM is still not able to provide the worthwhile information on the precise weight fraction of the sodium-rich phase and the composition of sodium-rich phase.

3.3. The relation between the fraction of four-coordinated boron and phase separation

The precise measurement of the sodium-rich phase was conducted by ^{11}B NMR in the present investigation. NMR spectroscopy has been an important tool in characterizing borate glass structure in recent years. In particular, the relative proportions of four- and three-coordinated boron can be qualified accurately using ^{11}B NMR. For sodium borate compounds, it was confirmed that there exits a direct linear relationship between the molar ratio of Na_2O vs B_2O_3 (R) and four-fold coordinated boron (N_4) when R is less than 0.5, because the addition of each sodium ion can lead to the formation of one $[BO_4]$-tetrahedral, as following illustrated:

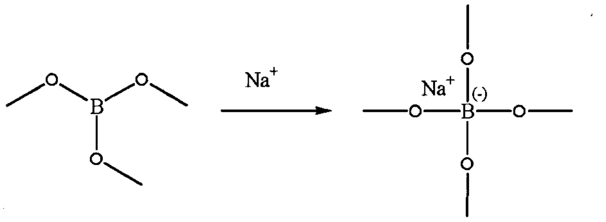

Illustration of the transformation of three-coordinated boron to four-coordinate boron by the addition of sodium oxide

When R is larger than 0.5, the linear relationship is broken and the N_4 decreases dramatically, as the addition of Na_2O would result in the formation of asymmetric $[BO_3]$ units with one non-bridge oxygen at the expense of $[BO_4]$ units[11–15]. The N_4 as a function of R (mol% Na_2O/mol% B_2O_3) in sodium borate glasses without phase separation measured by the pulse NMR in the present study is shown in Fig. 6. These NMR data coincide well with the results of previous research by Bray *et al.* [11–15]. The NMR spectra from the phase-separated glass will be more complex than that from the glass without phase separation because the former are overlapped by two phases. However, we can still analyze the composition of the sodium-rich phase by NMR spectra since the composition of the boron-rich phase is distinguished by XRD.

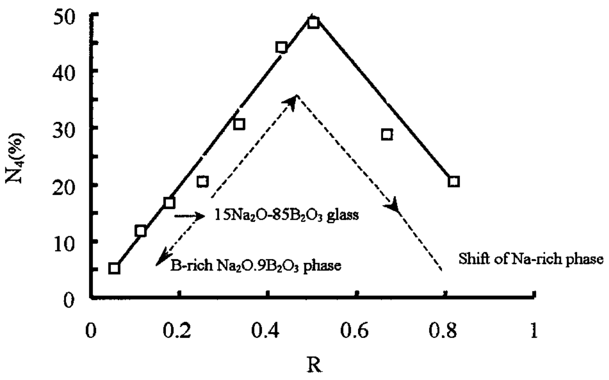

Figure 6 N_4 as a function of R for homogeneous Na_2O-B_2O_3 glasses.

For example, if Na-rich phase is $Na_2O{\cdot}4B_2O_3$ after phase separation, since the boron-rich phase has been distinguished as $Na_2O{\cdot}9B_2O_3$ by XRD, we get the following reaction model according to the mass balance:

$$\begin{aligned} &15Na_2O\text{-}85B_2O_3 \\ &\quad = 5(Na_2O{\cdot}9B_2O_3) + 10(Na_2O{\cdot}4B_2O_3) \end{aligned}$$

by Fig. 6, the fraction of four-coordinated boron in boron-rich $Na_2O{\cdot}9B_2O_3$ phase, $N_4^{(B)}$, is decreased to 11%. On the other hand, in Na-rich $Na_2O{\cdot}4B_2O_3$ phase, the fraction of four-coordinated boron, $N_4^{(Na)}$, is increased to 25%. The molar proportion of boron atoms between boron-rich $Na_2O{\cdot}9B_2O_3$ phase and Na-rich $Na_2O{\cdot}4B_2O_3$ phase could be calculated from above equation, which is 0.53 and 0.47 respectively. So, the fraction of four-coordinated boron in the phase-separated glass, N_4 value, would be:

$$\begin{aligned} N_4 &= 0.53N_4^{(B)} + 0.47N_4^{(Na)} \\ &= 0.53 \times 11 + 0.47 \times 25 \\ &= 18\% \end{aligned}$$

The NMR spectra of the samples with 0 h, 10 h, 20 h and 30 h of heat treatment at 500°C are shown in Fig. 7. Within 10 h of heat treatment, the areas corresponding to S_3 and S_4 exhibited little variation, while the time >10 h they changed significantly (Fig. 8). The results of quantitative calculations by fitting the NMR spectrum using computer software for NMR data processing program are shown in Table I. Theoretical calculation from some possible decomposed products, which are compared with the practical NMR measurement, is shown in Table III and Fig. 9. It can be seen from Table III that when the glass reaches equilibrium after 20 h heat treatment, the N_4 calculated from $3Na_2O{\cdot}B_2O_3$ agrees well with practical NMR measurement. This confirms that the sodium-rich phase at equilibrium is $3Na_2O{\cdot}B_2O_3$.

The NMR provides us an important method to measure the composition in the immiscible phases during phase separation since it has close relation with the change of structure. Within the heat treatment time range of 5–10 hours, it can be seen that N_4 value of the phase-separated glass by NMR measurement shows only a slight variation (Fig. 8). This corresponds to that the glass is separated into $Na_2O{\cdot}9B_2O_3$ phase and Na-rich residual phase in which the sodium ratio R is

TABLE III Comparison of N_4 values between theoretical calculation and experimental measurement by NMR during phase separation

Phase composition	Reaction model	N_4 by theoretical calculation (%)	N_4 by NMR measurement Value (%)	heat treatment time (hours)
Homogenous $15Na_2O.85B_2O_3$	x	18	17 ± 0.85	0
$Na_2O.9B_2O_3$, $Na_2O.4B_2O_3$	$15Na_2O.85B_2O_3 \rightarrow 5(Na_2O.9B_2O_3) + 10(Na_2O.4B_2O_3)$	18		
$Na_2O.9B_2O_3$, $Na_2O.3B_3O_3$	$15Na_2O.85B_2O_3 \rightarrow 6.67(Na_2O.9B_2O_3) + 8.33(Na_2O.3B_2O_3)$	18	~ 16 ± 0.80	5–10
$Na_2O.9B_2O_3$, $Na_2O.2B_2O_3$	$15Na_2O.85B_2O_3 \rightarrow 7.86(Na_2O.9B_2O_3) + 7.14(Na_2O.2B_2O_3)$	18		
$Na_2O.9B_2O_3$, $3Na_2O.B_2O_3$	$15Na_2O.85B_2O_3 \rightarrow 9.23(Na_2O.9B_2O_3) + 1.92(3Na_2O.B_2O_3)$	$\simeq 10$	$10 \sim 11$ ± 0.50	>20

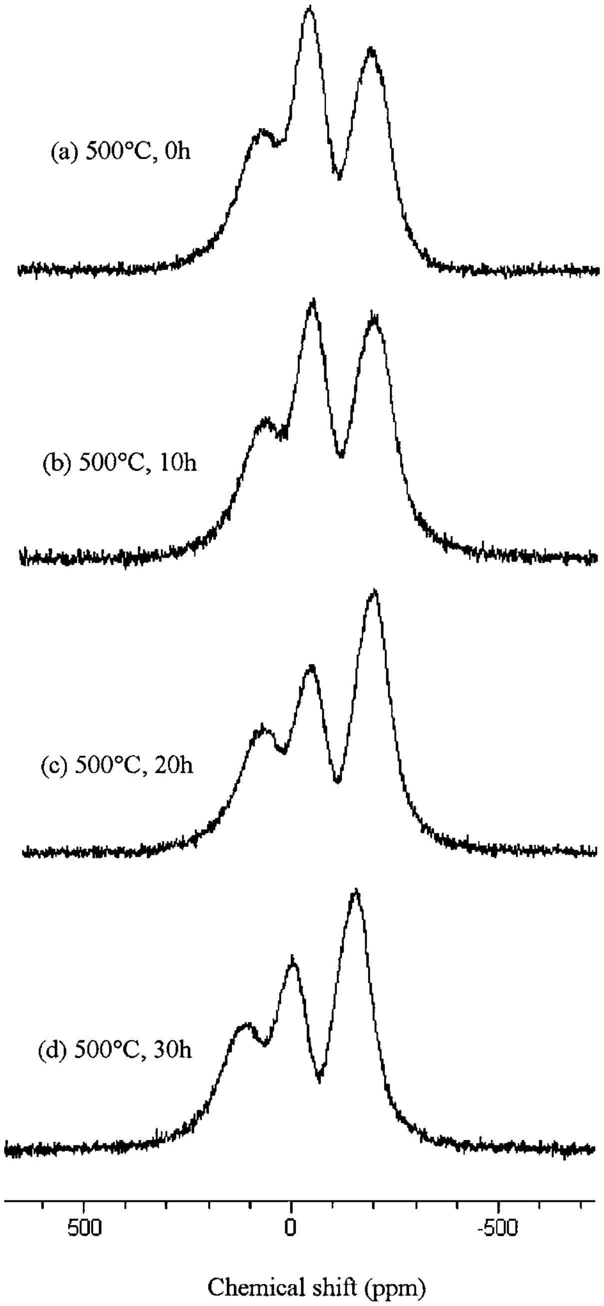

Figure 7 ^{11}B NMR spectra of $15Na_2O$-$85B_2O_3$ samples after heat treatment.

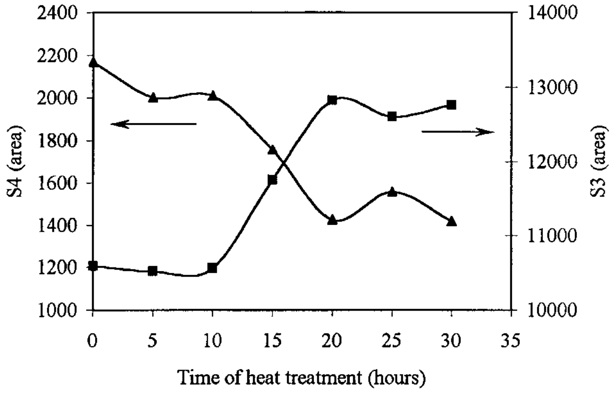

Figure 8 The dependence of S_3 and S_4 areas on heat treatment time.

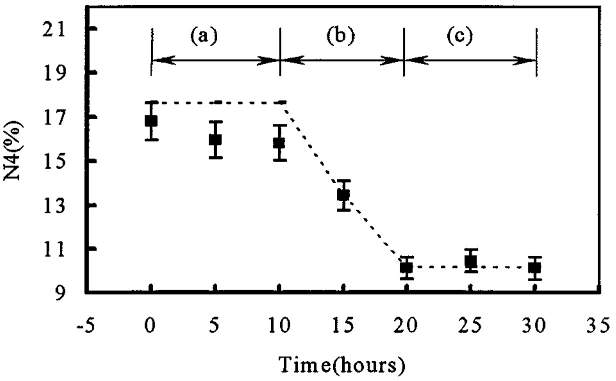

Figure 9 N_4 variation from NMR measurement corresponding to different composition of separated phase during heat treatment at 500°C (dash line is theoretical N_4 value calculated from Table III). (a) Boron-rich phase: $Na_2O{\cdot}9B_2O_3$; Sodium-rich phase: $RNa_2O{\cdot}B_2O_3$, $R < 0.5$, (b) Boron-rich phase: $Na_2O{\cdot}9B_2O_3$; Sodium-rich phase: $RNa_2O{\cdot}B_2O_3$, $0.5 < R < 3$, (c) Boron-rich phase: $Na_2O{\cdot}9B_2O_3$; Sodium-rich phase: $RNa_2O{\cdot}B_2O_3$, $R = 3$.

less than 0.5. When R is less than 0.5, the addition of each sodium ion can lead to the formation of one (BO_4)-tetrahedral. Therefore, there exits a direct linear relationship between sodium content and N_4 in each phase. As shown in Fig. 6, Na_2O-$9B_2O_3$ has lower N_4 value as compared with $15Na_2O$-$85B_2O_3$, and on the other hand, Na-rich residual phase has higher N_4 value.

Consequently, the N_4 value of the phase-separated glass by averaging that of the $Na_2O{\cdot}9B_2O_3$ phase and the Na-rich phase should not have great difference from the original glass (Fig. 9).

However, within the heat treatment time range of 10–20 hours, N_4 value decreased dramatically (Fig. 9). This range corresponded to that glass is separated into $Na_2O{\cdot}9B_2O_3$ phase and the Na-rich residual phase in which the sodium ratio R is larger than 0.5. Within the composition range of $R > 0.5$, the direct linear relationship between sodium content and N_4 was broken (Fig. 6), as the addition of Na_2O would result in the formation of asymmetric $[BO_3]$ units with one non-bridge oxygen at the expense of $[BO_4]$ units [10, 11, 15]. So, the N_4 value of the Na-rich residual phase decreased rapidly. As both the $Na_2O{\cdot}9B_2O_3$ phase and Na-rich amorphous phase contributed to the decrease of the N_4 value respectively, the average N_4 value of the immiscible two phases also decreased rapidly with further heat treatment. For example, when $15Na_2O\text{-}85B_2O_3$ was separating into boron-rich $Na_2O{\cdot}9B_2O_3$ phase and Na-rich $3Na_2O{\cdot}B_2O_3$ phase:

$$\begin{aligned}&15Na_2O\text{-}85B_2O_3\\&\quad\rightarrow 9.23(Na_2O{\cdot}9B_2O_3) + 1.92(3Na_2O{\cdot}B_2O_3) \qquad (6)\end{aligned}$$

As can be seen in Fig. 6, in boron-rich $Na_2O{\cdot}9B_2O_3$ phase, the fraction of four-coordinated boron, $N_4^{(B)}$, is decreased to 11%. On the other hand, in Na-rich $3Na_2O{\cdot}B_2O_3$ phase, the fraction of four-coordinated boron, $N_4^{(Na)}$, is also dramatically decreased to near 0. The proportion of boron atoms between boron-rich $Na_2O{\cdot}9B_2O_3$ phase and Na-rich $3Na_2O{\cdot}B_2O_3$ phase, which was determined by the Equation 6, was 0.92 and 0.08 respectively. So, the fraction of four-coordinated boron in phase-separated sample, N_4 value, would be:

$$\begin{aligned}N_4 &= 0.92N_4^{(B)} + 0.08N_4^{(Na)}\\&\approx 0.92 \times 11 + 0.08 \times 0\\&= 10\%\end{aligned}$$

The fraction of four-coordinated boron in the phase-separated glass should decrease about 36% as compared with $15Na_2O\text{-}85B_2O_3$ original glasses, which coincided well with our NMR measurement for the sample with 20 h of heat treatment. The weight percent of boron-rich $Na_2O{\cdot}9B_2O_3$ phase in the phase-separated sample, calculated from Equation 6, should reach 0.93. So, it is not surprising that the peaks of $3Na_2O{\cdot}B_2O_3$ crystal phase were weak (see Fig. 3), as the weight percent of the $3Na_2O{\cdot}B_2O_3$ crystal phase takes only 7%. The NMR measurement results also coincide well with SEM photograph. The SEM photograph, as shown in Fig. 5, exhibited that the sample mainly composed of the $Na_2O{\cdot}9B_2O_3$ crystal after 20 h heat treatment. Small-size $3Na_2O{\cdot}B_2O_3$ crystal with the amount percent of 5–10% was distributed among the $Na_2O{\cdot}9B_2O_3$ crystal phase.

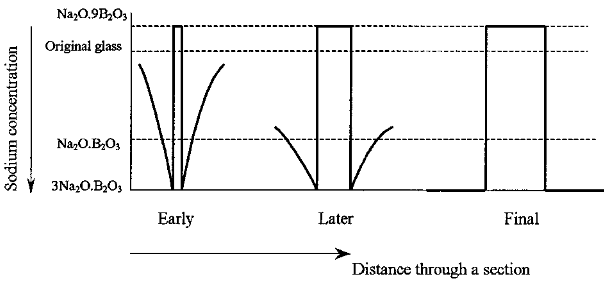

Figure 10 Illustration of the variation of the composition in immiscible phases during phase separation in sodium borate glasses.

4. Discussion

The present investigation on the decomposition products in $15Na_2O\text{-}85B_2O_3$ binary glass at 500°C suggests that the phase equilibrium is controlled by the crystal growth rate of the boron-rich phase and the sodium-rich phase. The phase equilibrium in $15Na_2O\text{-}85B_2O_3$ binary glass takes long time due to the difficulty in crystallization of sodium-rich phase. The investigation indicates that, at first, the growth of the $Na_2O{\cdot}9B_2O_3$ phase consumes boron oxide from the matrix, resulting in that the residual glass is forced to high concentrations of sodium oxide during phase separation. When the molar ratio of Na_2O versus B_2O_3 in the residual glass reaches 1 : 4, it is assumed that the nucleation and crystal growth rate of the $Na_2O{\cdot}4B_2O_3$ is slower than that of $Na_2O{\cdot}9B_2O_3$. Thus the $Na_2O{\cdot}9B_2O_3$ will continue to grow, forcing the residual glass to much higher concentrations of sodium oxide rather than crystallizing as $Na_2O{\cdot}4B_2O_3$ crystal and reaching equilibrium as suggested by the phase diagram [8, 9]. Fig. 10 illustrates the schematic variation of the composition in the immiscible phases during phase separation.

Prabakar and Rao [23] have found that at some topologically feasible positions in sodium borate binary glasses, three-coordinated borons and two-coordinated oxygens get coupled forming BO_4 and BO_3 units, resulting in the formation of the over-coordination of oxygen atoms, as shown bellow:

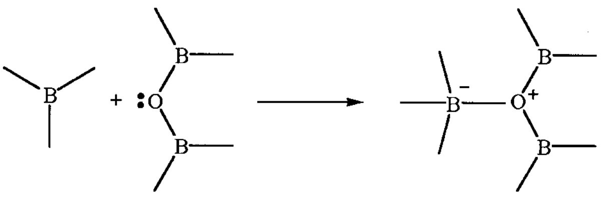

Illustration of the formation of the over-coordination of oxygen atom

From the point of the view in topochemistry, the formation of the over-coordination will cause a staggering of B-O chains. The over-coordinated oxygen atoms where they coordinated trigonal borons are positioned in other layers where tetrahedral borons are simultaneously coordinated by the over-coordinated oxygen atoms. The staggering of the B-O chains caused by such over-coordination of oxygen atoms is very inimical to crystallization. It was found by Prabakar and Rao [23] that the tendency of the conversion of some of trigonal borons to the tetrahedral borons through the over-coordination is especially strong in the 10–33 mol% alkali oxide region. Thus the boron-rich phase can readily crystallize at $Na_2O{\cdot}9B_2O_3$ where the concentration of the over-coordinated oxygen atoms is very low, while the sodium-rich phase does not crystallize and reach equilibrium at $Na_2O{\cdot}4B_2O_3$ as suggested by the phase diagram [8, 9] where the concentration of the over-coordinated oxygen atoms is high. Above 33 mol% alkali, tetrahedral borons are gradually converted to trigonal borons. The over-coordinated oxygen atoms are also gradually exhausted with the decrease in tetrahedral borons. The over-coordinated oxygen atoms are assumed to be completely used up at $3Na_2O{\cdot}B_2O_3$ where tetrahedral borons are all converted to trigonal borons. Consequently, when the molar ratio of Na_2O versus B_2O_3 in the residual glass reaches 3 : 1, it is thought that the nucleation and crystal growth rate of the $3Na_2O{\cdot}B_2O_3$ becomes higher than that of $Na_2O{\cdot}9B_2O_3$. Therefore, the $3Na_2O{\cdot}B_2O_3$ is able to crystallize. As a result, $Na_2O{\cdot}9B_2O_3$ stops to grow and the phase equilibrium is finally reached at this sodium-rich composition.

The sodium borate materials with higher sodium content than 50% in the form of single phase usually exhibits hygroscopic property and cannot exist as glass at room temperature. It should be noticed that this is true only in case of the homogeneous single phase at room temperature. Let's think when the glass is going to separate into $Na_2O{\cdot}B_2O_3$ (50% Na_2O) according to the following reaction model:

$$15Na_2O \cdot 85B_2O_3 \\ \rightarrow \frac{35}{4}(Na_2O \cdot 9B_2O_3) + \frac{25}{4}(Na_2O \cdot B_2O_3)$$

It is easy to calculate the weight fraction of Na2O·B2O3 phase. The calculation result shows that the weight fraction of Na2O·B2O3 takes only 12%. Further more, the higher the sodium content in Na-rich phase, the smaller the fraction of Na-rich phase takes. Considering that this small amount of Na-rich phase (12% or less than 12%) is wrapped by 88% (or larger than 88%) of Na2O·9B2O3 boron-rich phase, it is considered that the direct touch of Na2O·B2O3 phase (or Na-rich phase) with humidity is greatly inhibited. Thus, the Na-rich amorphous phase with continuously shifting toward higher sodium oxide concentration is possible during phase separation.

5. Conclusions

1. The equilibrium of the phase separation in $15Na_2O$-$85B_2O_3$ glass takes long time due to the difficulty in crystallizing Na-rich phase. The phenomena may be caused by over-coordination of oxygen atoms formed in the conversion of some of trigonal borons to the tetrahedral borons during phase separation.

2. The final composition of the separated phase depended upon the rate competition of the nucleation and crystal growth between the two immiscible phases rather than those being proposed by the conventional phase diagram. When the growth rate of the $Na_2O{\cdot}9B_2O_3$ crystal is higher, the residual sodium-rich phase will be forced to higher concentration of sodium oxide. Otherwise, the residual sodium-rich phase will crystallize and consequently the phase equilibrium is reached. For $15Na_2O$-$85B_2O_3$ glasses, sample at first separated out $Na_2O{\cdot}9B_2O_3$ phase. The composition of Na-rich residual phase was always fluctuating during heat treatment until its molar ratio of Na_2O versus B_2O_3 reached 3 : 1.

3. At the initial stage of phase separation, the fraction of the fourfold-coordinated boron in samples showed little variation due to the interaction of the two immiscible phases, i.e., $Na_2O{\cdot}9B_2O_3$ phase and Na-rich residual phase. Although the fraction of the four-coordinated boron actually decreased in $Na_2O{\cdot}9B_2O_3$ phase, it increased in Na-rich residual phase. The average value from the immiscible two phases exhibited little of effect.

4. With the propagation of the phase separation, significant effect of decrease in the fraction of four-coordinated boron in the heat-treated samples was observed. This phenomenon was caused by the continuous shift of sodium content higher than $R = 0.5$ in Na-rich residual phase. When the sodium/boron ratios in Na-rich residual phase shifted higher than 0.5, lots of $[BO_3]$ units with one non-bridge oxygen were formed at the expense of four-coordinated boron, resulting in the dramatic decrease in the fraction of four-coordinated boron. The NMR patterns provide us an important method to analyse the composition of the immiscible phases during phase separation.

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