

RAPID COMMUNICATION

Study of Phase Separation in Na₂O–B₂O₃ Glass System by Nuclear Magnetic ResonanceWei-Fang Du,^{*,1} Koji Kuraoka,[†] Tomoko Akai,[†] and Tetsuo Yazawa[†]^{*}New Energy and Industrial Technology Development Organization, Midorigaoka 1-8-31, Ikeda City, Osaka 563-8577, Japan; and[†]Optical Materials Department, Osaka National Research Institute, Midorigaoka 1-8-31, Ikeda City, Osaka 563-8577, Japan

Received July 7, 1999; in revised form October 18, 1999; accepted November 5, 1999

The ¹¹B nuclear magnetic resonance (NMR) spectra, together with X-ray diffraction (XRD) and scanning electron microscopy (SEM), have been used to investigate the phase separation in 15Na₂O–85B₂O₃ binary glass. Based on the present investigation we suggest that the phase equilibrium in sodium borate glasses is controlled by the rate competition of the nucleation and crystal growth between two immiscible phases rather than those being proposed by the conventional phase diagram. The experimental results show that the sodium-rich phase, after being heat-treated at 500°C, was not Na₂O.4B₂O₃, as indicated by phase diagram. The over-coordination of oxygen atoms in the sodium-rich phase rendered difficulties in the crystallization of the sodium-rich phase with less than 75 mol % sodium oxide. Therefore, the high growth rate of the boron-rich phase can force the residual glass toward much higher concentrations of sodium oxide. According to the NMR measurements, it was found that, after reaching equilibrium, the 15Na₂O–85B₂O₃ glass separated into Na₂O.9B₂O₃ and 3Na₂O.B₂O₃. © 2000 Academic Press

1. INTRODUCTION

Phase separation is a key step for the preparation of sodium borosilicate porous glass (1–4), which is finding widespread application in separation membrane, enzyme and catalyst support, photonics, etc. (1). As sodium cations preferentially associate themselves with the borate network in sodium borosilicate glasses (5–7), the sodium ions may migrate to those groups in which boron is subject to latent conditions for separation during heat treatment. This migration of the sodium ions results in a local accumulation of

cations and subsequent preseparation in the Na₂O–B₂O₃ system, which would lead to the final separation of a boron-rich phase and of a SiO₂-rich phase in sodium borosilicate ternary glasses (5). From the point of view in materials design, it is very important to clarify the phase equilibrium in binary Na₂O–B₂O₃ glass because the composition and pore characteristics of the porous glass is closely related to the phase separation in the sodium borate system.

The sodium borosilicate glass with a ratio of Na₂O : B₂O₃ \cong 15 : 85 exhibits the strongest tendency toward phase separation (5). Concerning the Na₂O–B₂O₃ binary system, it is usually thought that the decomposition of the 15Na₂O–85B₂O₃ glass leads to product close to the original composition during heat treatment. The phase diagram of the binary Na₂O–B₂O₃ system shows that the phase equilibrium for 15Na₂O–85B₂O₃ remains between Na₂O.9B₂O₃ and Na₂O.4B₂O₃ (8–9). However, these data of the phase equilibrium of the binary Na₂O–B₂O₃ 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 process of the phase separation in Na₂O–B₂O₃ glasses by several techniques, including nuclear magnetic resonance. We present new data of the phase equilibrium at 500°C, which suggested that it is difficult to crystallize sodium-rich phases due to the over-coordination of oxygen atoms. The phase equilibrium in sodium borate glasses is controlled by the competition between the rates of nucleation and crystal growth involving two immiscible phases that differ from those of the conventional phase diagram.

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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 min. The melts were poured into carbon molds. For those samples for which sodium content is larger than 33.3%, the melt was poured onto a metal plate and quickly covered with a brass block. The samples were transparent and showed no sign of devitrification when checked by X-ray diffraction techniques. The samples were immediately placed in a sealed plastic bag inside a humidistat to ensure they were not degraded by humidity. The glass transition temperature is about 400°C (5). A phase separation was carried out at $400\text{--}550^\circ\text{C}$ for 5–30 h.

2.2. NMR, XRD, and SEM Measurements

The ^{11}B NMR experiments were performed at 64.19 MHz. The spectra were obtained by Fourier transforming the free-induction decay. The length of the 90° pulses was set to $4.5\ \mu\text{s}$ by using a H_3BO_3 solution. In the measurement we used a pulse as short as $1\ \mu\text{s}$ to avoid the distortion of the spectra from quadrupole effects (10). Typically, 64 scans were used to obtain the spectra. The structure of the glass containing boron have been extensively studied by NMR by many of researchers (11–21). It has been shown that boron atoms exist in either threefold or fourfold coordination with the oxygen network. As shown in Fig. 1, the spectrum areas of S_3 and S_4 are proportional to the number of fourfold- and threefold-coordinated boron atoms, respectively.

The pulse-FTNMR method employed in recent NMR spectrometer experiments is usually more convenient than the continuous wave method which had been used until the 1970s. 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 the time domain. 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 $x\text{Na}_2\text{O}-(1-x)\text{B}_2\text{O}_3$ glasses, where the fraction of the four-coordinated boron (N_4) is well known to be $x/(1-x)$ (11), and thereby determined the calibration factor. We also measured $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses and some sodium borate crys-

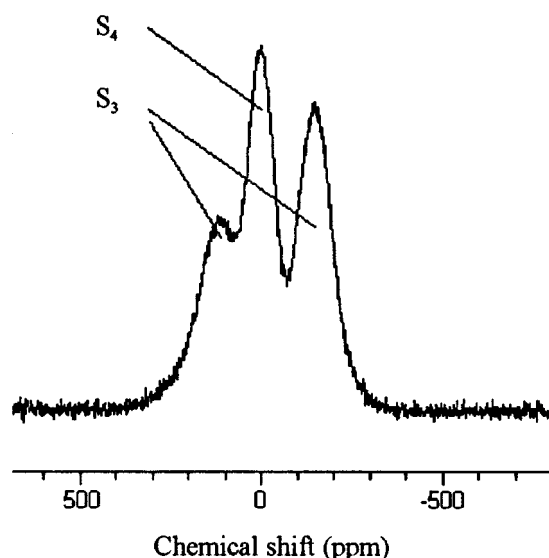


FIG. 1. Pulse NMR spectrum of the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ sample. The absorption curve corresponds to the resonance from threefold- and fourfold-coordinated boron, respectively.

tals and confirmed that this calibration factor can be used over a wide compositional range.

X-ray diffraction (XRD) patterns were recorded with $\text{CuK}\alpha$ radiation at a scanning step of 0.1 in the 2θ range $5\text{--}60$, under operating 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 AND DISCUSSION

Figure 2 shows the X-ray diffraction patterns of the $15\text{Na}_2\text{O}-85\text{B}_2\text{O}_3$ samples with different time of heat treatment. It is interesting to note that: (1) When the heat treatment time is shorter than 20 h, the X-ray diffraction peaks coincide very well with $\text{Na}_2\text{O}\cdot 9\text{B}_2\text{O}_3$ crystals, which indicates that the boron-rich phase of the decomposed products is $\text{Na}_2\text{O}\cdot 9\text{B}_2\text{O}_3$. It can be deduced that the sodium-rich phase is still amorphous. In addition, the intensity of the peaks increases with heat treatment time, which suggests that the amount of the $\text{Na}_2\text{O}\cdot 9\text{B}_2\text{O}_3$ boron-rich phase increases with in the course of the phase separation and that phase equilibrium still is not reached. (2) When the heat treatment time reached 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 $\text{Na}_2\text{O}\cdot 9\text{B}_2\text{O}_3$.

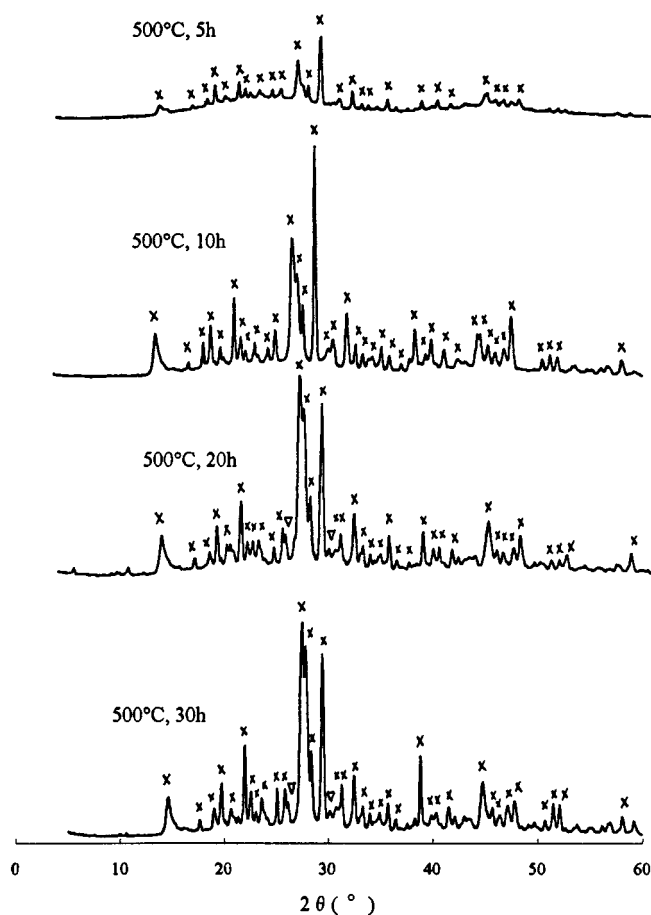
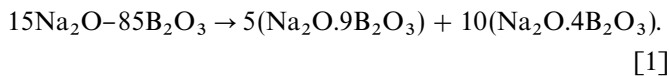


FIG. 2. XRD patterns of $15\text{Na}_2\text{O}-85\text{B}_2\text{O}_3$ glass after heat treatment: (x) $\text{Na}_2\text{O}\cdot 9\text{B}_2\text{O}_3$ crystal, (v) new crystal.

It is very difficult completely to distinguish the new diffraction peaks after 20 h of heat treatment as a large number of these diffraction peaks are very weak. In addition, many of the sodium borate compounds, such as $\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}\cdot \text{B}_2\text{O}_3$, and $3\text{Na}_2\text{O}\cdot \text{B}_2\text{O}_3$, have similar diffraction peaks along with the new diffraction peaks, which makes it difficult to distinguish the various compounds. The phase diagram suggests that the $15\text{Na}_2\text{O}-85\text{B}_2\text{O}_3$ glass decomposes into $\text{Na}_2\text{O}\cdot 9\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$, according to the reaction model (8–9).

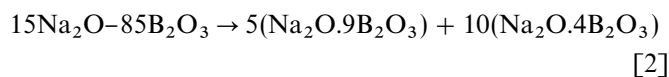


This reaction model for the phase separation shows that the weights of the boron-rich phase and sodium-rich phases are nearly 50%, respectively. Because of the similarity in densities of the boron-rich phase and the sodium-rich phase which contain small amounts of sodium, the volume of the boron-rich phase and sodium-rich phase may also be assumed to

be close to 50%, respectively. However, the SEM observation of the present investigation, as shown in Fig. 3, does not agree with the above phase separation model. The SEM photograph coincides well with our XRD data. It can be seen from Fig. 3 that when the heat treatment time is shorter than 20 h, the $\text{Na}_2\text{O}\cdot 9\text{B}_2\text{O}_3$ crystal at first grows gradually from the matrix glass. Then the residual sodium-rich glass crystallizes after 20 h 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. According to mass balance, this small amount of boron-rich phase should have much higher content of sodium oxide than $\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$ suggested by phase diagram. However, since the microstructure of the separated phases is anisotropic (Fig. 3), the result of the linear analysis of the SEM photograph should be very rough. The SEM are still not able to provide the worth while information on the precise weight fraction of the sodium-rich phase and the composition of the sodium-rich phase.

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. It was confirmed that there exists a direct linear relationship between the molar ratio of Na_2O vs B_2O_3 (R) and four-fold coordinated boron (N_4) for sodium borate compounds when R is less than 0.5, as the addition of each sodium oxide can lead to the formation of one (BO_4) -tetrahedra. When R is larger than 0.5, the linear relationship is broken and the N_4 decreases dramatically, since the addition of Na_2O would result in the formation of asymmetric $[\text{BO}_3]$ units with one nonbridge oxygen at the expense of $[\text{BO}_4]$ units (10–12, 17). The N_4 as a function of R (mol% Na_2O /mol% B_2O_3) measured by pulse NMR in the present study is shown in Fig. 4. These NMR data from the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ glass without phase separation 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 phase. 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.

For example, if the Na-rich phase is $\text{Na}_2\text{O}\cdot 4\text{B}_2\text{O}_3$ after phase separation, since the boron-rich phase has been distinguished as $\text{Na}_2\text{O}\cdot 9\text{B}_2\text{O}_3$ by XRD, we get the following reaction model according to the mass balance



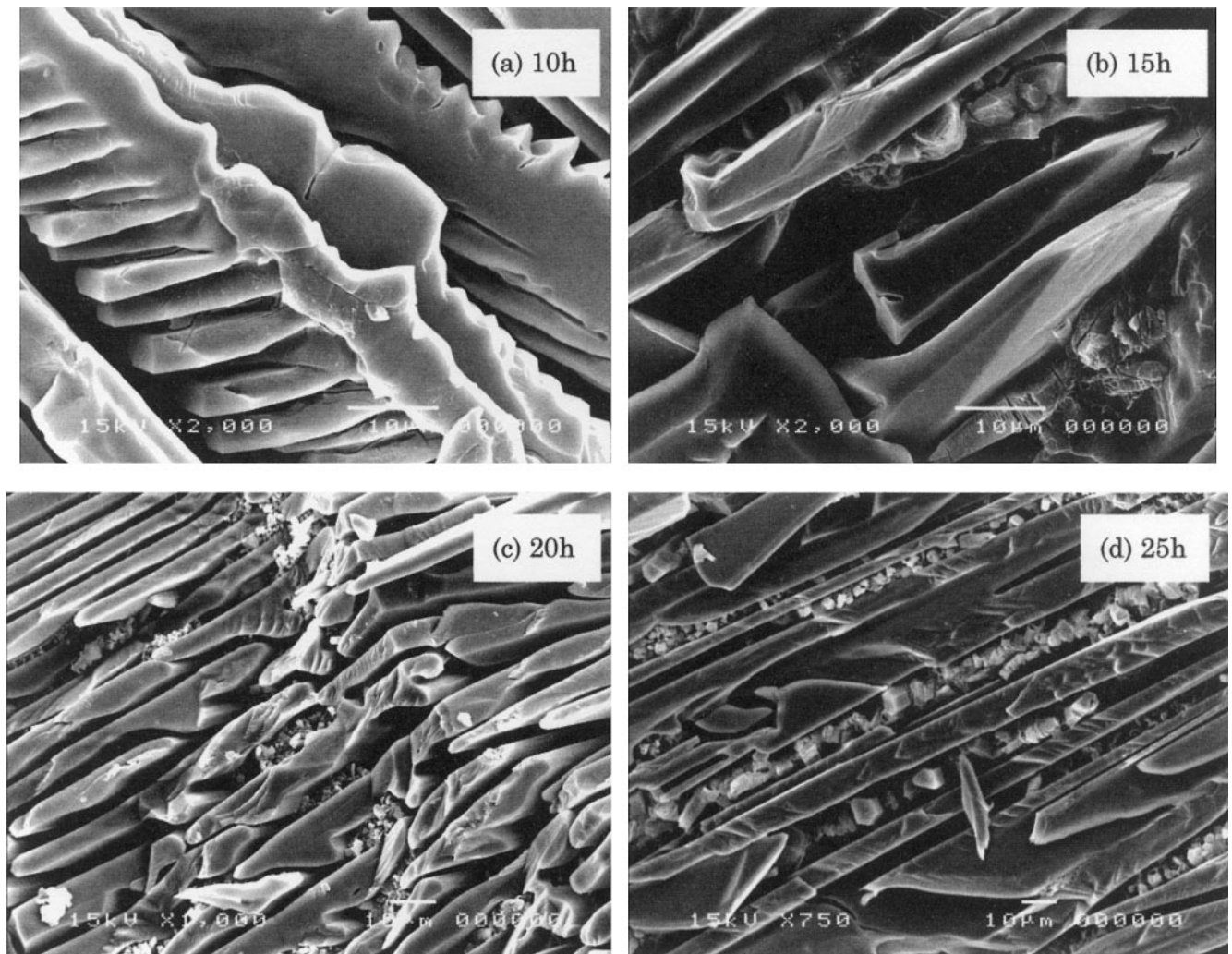


FIG. 3. SEM photographs of the samples with different heat treatment time.

by Fig. 4, fraction of four-coordinated boron in boron-rich $\text{Na}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3$ phase, $N_4^{(B)}$, is decreased to 11%. In contrast, in the Na-rich $\text{Na}_2\text{O} \cdot 0.4\text{B}_2\text{O}_3$ phase, the fraction of four-coordinated boron, $N_4^{(Na)}$, is increased to 25%. The molar proportion of boron atoms between the boron-rich $\text{Na}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3$ phase and the Na-rich $\text{Na}_2\text{O} \cdot 0.4\text{B}_2\text{O}_3$ phase could be calculated from the reaction model [2], 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

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

The NMR spectra of the samples with 0, 10, 20, and 30 h of heat treatment at 500°C are shown in Fig. 5. Theoretical

calculation from some possible decomposed products, which are compared with the practical NMR measurement, is shown in Table 1. It can be seen from Table 1 that when the glass reaches equilibrium after 20 h heat treating, the N_4 calculated from $3\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ agrees well with the practical NMR measurement. This confirms that the sodium-rich phase at equilibrium is $3\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$.

The present investigation on the decomposition products in $15\text{Na}_2\text{O} - 85\text{B}_2\text{O}_3$ 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 $15\text{Na}_2\text{O} - 85\text{B}_2\text{O}_3$ binary glass takes a long time due to the difficulty in crystallization of the sodium-rich phase. The investigation indicates that, at first, the growth of the $\text{Na}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3$ phase consumes boron oxide from the matrix, resulting in the residual glass being forced to high concentrations of sodium oxide during phase separation. When the molar ratio of Na_2O versus B_2O_3 in the

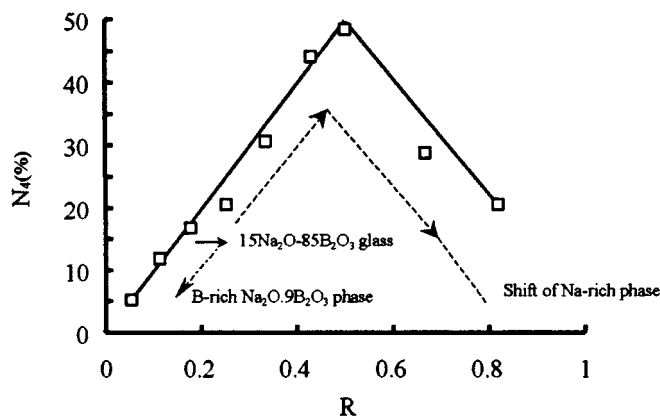


FIG. 4. The fraction of four-coordinated boron (N_4) as a function of the molar ratio of Na_2O vs B_2O_3 (R) for Na_2O - B_2O_3 glasses without phase separation.

residual glass reaches 1:4, it is assumed that the nucleation and crystal growth rate of the $\text{Na}_2\text{O}.4\text{B}_2\text{O}_3$ is slower than that of $\text{Na}_2\text{O}.9\text{B}_2\text{O}_3$. Thus the $\text{Na}_2\text{O}.9\text{B}_2\text{O}_3$ will continue to grow, forcing the residual glass to much higher concentrations of sodium oxide, rather than crystallizing as $\text{Na}_2\text{O}.4\text{B}_2\text{O}_3$ crystal and reaching equilibrium as suggested by the phase diagram (8). Prabakar and Rao (16) 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. 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 are very inimical to crystallization. It was found by Prabakar and Rao (16) that the tendency of the conversion of some of the 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 $\text{Na}_2\text{O}.9\text{B}_2\text{O}_3$, where the concentration of the over-coordinated oxygen atoms is very low, while the sodium-rich phase does not crystallize and reach equilibrium at $\text{Na}_2\text{O}.4\text{B}_2\text{O}_3$ as suggested by the phase diagram (8), 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 in $3\text{Na}_2\text{O}. \text{B}_2\text{O}_3$, 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 $3\text{Na}_2\text{O}. \text{B}_2\text{O}_3$ becomes higher than that of $\text{Na}_2\text{O}.9\text{B}_2\text{O}_3$. Therefore, the $3\text{Na}_2\text{O}. \text{B}_2\text{O}_3$ is able to crystallize. As a result, $\text{Na}_2\text{O}.9\text{B}_2\text{O}_3$ stops to grow and the phase equilibrium is finally reached at this sodium-rich composition.

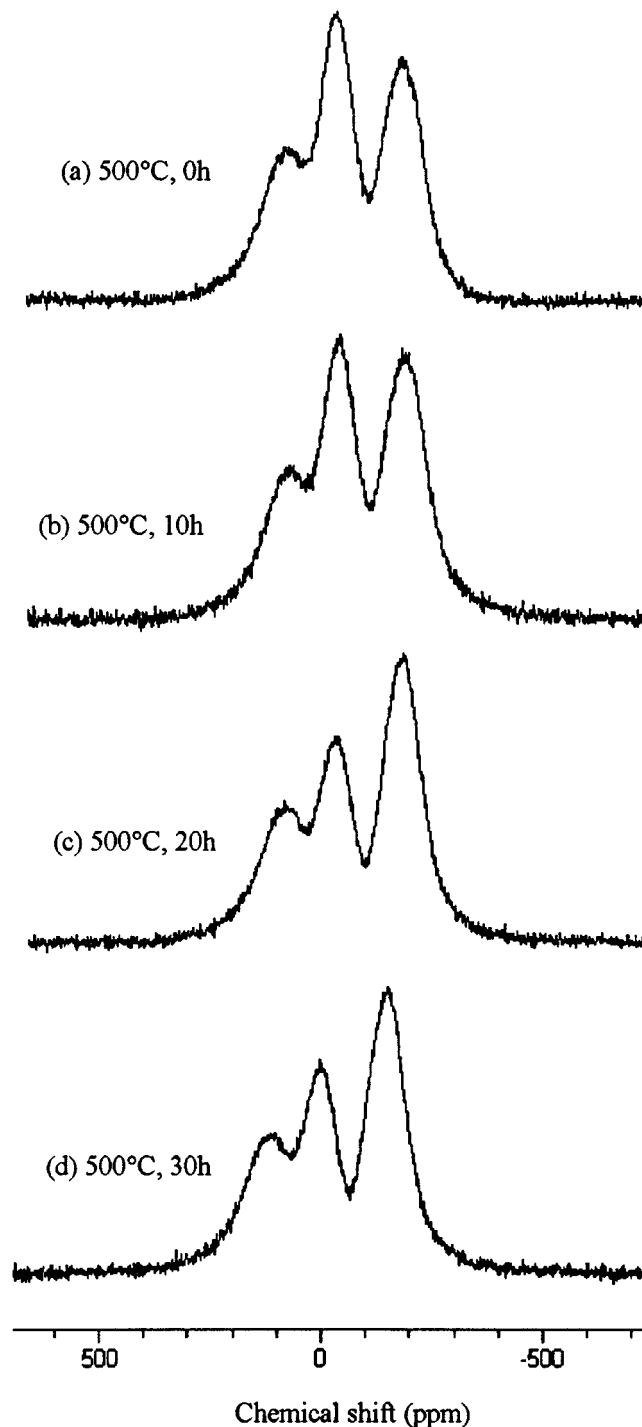


FIG. 5. NMR spectra of $15\text{Na}_2\text{O}-85\text{B}_2\text{O}_3$ samples after different heat treatment conditions.

TABLE 1
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 (h)
Homogeneous $15\text{Na}_2\text{O}-85\text{B}_2\text{O}_3$	×	18	17 ± 0.85	0
$\text{Na}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3$, $\text{Na}_2\text{O} \cdot 0.4\text{B}_2\text{O}_3$	$15\text{Na}_2\text{O}-85\text{B}_2\text{O}_3 \rightarrow 5(\text{Na}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3) + 10(\text{Na}_2\text{O} \cdot 0.4\text{B}_2\text{O}_3)$	18		
$\text{Na}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3$, $\text{Na}_2\text{O} \cdot 0.3\text{B}_2\text{O}_3$	$15\text{Na}_2\text{O}-85\text{B}_2\text{O}_3 \rightarrow 6.67(\text{Na}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3) + 8.33(\text{Na}_2\text{O} \cdot 0.3\text{B}_2\text{O}_3)$	18	~16 ± 0.80	5-10
$\text{Na}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3$, $\text{Na}_2\text{O} \cdot 0.2\text{B}_2\text{O}_3$	$15\text{Na}_2\text{O}-85\text{B}_2\text{O}_3 \rightarrow 7.86(\text{Na}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3) + 7.14(\text{Na}_2\text{O} \cdot 0.2\text{B}_2\text{O}_3)$	18		
$\text{Na}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3$, $3\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$	$15\text{Na}_2\text{O}-85\text{B}_2\text{O}_3 \rightarrow 9.23(\text{Na}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3) + 1.92(3\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3)$	≈ 10	10 ± 0.50	> 20

4. CONCLUSIONS

1. $15\text{Na}_2\text{O}-85\text{B}_2\text{O}_3$ binary glass is finally separated into a $\text{Na}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3$ phase and a $3\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$ phase at 500°C according to the NMR spectra.

2. The phase equilibrium of the decomposed sodium borate glass are controlled by 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 $\text{Na}_2\text{O} \cdot 0.9\text{B}_2\text{O}_3$ crystal is higher, the residual sodium-rich phase will be forced to a higher concentration of sodium oxide. Otherwise, their residual sodium-rich phase will crystallize and consequently the phase equilibrium is reached.

3. Sodium-rich phase with less than 75% sodium oxide shows difficulty in crystallization during the process of phase separation. The phenomena may be caused by over-coordination of oxygen atoms formed on the conversion of some of the trigonal borons to the tetrahedral borons during phase separation.

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