*Journal of the Korean Magnetic Resonance Society* **2005**, *9*, 61 - 66

# Investigation of $xV_2O_5$-$B_2O_3$ and $xV_2O_5$-$B_2O_3$-$yNa_2O$ Glasses by $^{11}B$ MAS NMR

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*Received March 29, 2005*

***Abstract:*** $^{11}B$ MAS NMR spectra of binary glass system $xV_2O_5$-$B_2O_3$ and ternary glass system $xV_2O_5$-$B_2O_3$-$yNa_2O$ (x = $V_2O_5$ mol%/$B_2O_3$ mol%, y = $Na_2O$ mol%/$B_2O_3$ mol%) were acquired. $BO_3$ units are dominant components in the spectra of $xV_2O_5$-$B_2O_3$ glass systems while both $BO_3$ and $BO_4$ units appear in comparable amounts in the spectra of $xV_2O_5$-$B_2O_3$-$yNa_2O$ glass systems. More $BO_3$ units were monitored for higher $V_2O_5$ contents while more $BO_4$ units for higher $Na_2O$ contents. Quadrupole parameters such as $e^2qQ$ and $\eta$ obtained from spectral simulation indicate that $e^2qQ$ has a maximum value at x = y = 1 and $\eta$ decreases and increases as x or y grows, respectively. Our results suggest that $V_2O_5$ and $Na_2O$ play opposite roles in the ternary glasses.

Keywords : $^{11}B$ NMR, ternary glass, $BO_3$, $BO_4$

## INTRODUCTION

Oxide glass is also called as network-forming oxide since it forms random networks in 3-dimension. Representative network-forming oxides are $B_2O_3$, $SiO_2$, $GeO_2$[1]. Since the report by Denton et al. that oxide glass with transition metal ions has semiconducting properties[2], it was discovered that the conduction in the oxide glass is by electron rather than ions[3,4]. $V_2O_5$ was known as a good glass former to produce homogeneous glass[5].

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Nuclear Magnetic Resonance (NMR) has been excellent to probe local structures at boron sites in glass samples. However, $^{11}B$ is a quadrupole nucleus with spin number of 3/2 bringing out broad line widths. This low spectral resolution results in high uncertainties in measuring quadrupole parameters such as quadrupole coupling constant ($e^2qQ$) and asymmetry parameter ($\eta$) as well as chemical shift. Thus we obtained relative intensities of $BO_4$ and $BO_3$ units in addition to quadrupole parameters by employing Magic Angle Spinning (MAS). $e^2qQ$ represents the maximum magnitude of electric field gradients at the site of observed nuclei while $\eta$ does the deviation of the electric field gradient at the site from axial symmetry in the principal axis system.

$^{11}B$ MAS NMR spectra of binary glass system $xV_2O_5$-$B_2O_3$ and $Na_2O$ added ternary glass system $xV_2O_5$-$B_2O_3$-$yNa_2O$ were acquired. From the spectrum simulation, variation of quadrupole parameters as well as relative intensities of $BO_4$ and $BO_3$ units as a function of x and y were studied. Present work can deepen our understanding of local structures in glass by characterizing local environment around boron sites in glass.

## EXPERIMENTAL

### *Materials*

Ternary glass samples were prepared with $B_2O_3$ as a glass former, $V_2O_5$ as a transition metal ion unit, and $Na_2O$ as an alkaline metal unit. 8 samples with different compositions are prepared as summarized in Table 1 where x = $V_2O_5$ mol%/$B_2O_3$ mol% and y = $Na_2O$ mol%/$B_2O_3$ mol%. $Na_2CO_3$, $H_3BO_3$, and $V_2O$ reagents were purchased from Aldrich and appropriate amounts of the chemicals were well mixed and then dried in a vacuum oven at 150°C for 15 mins. Dried mixture samples were melted in Pt crucibles in an electric furnace (Linberg Co. Model 51333) at the temperature of 1000 ~ 1100°C. Melt was kept for 30 mins and rapidly quenched on stainless steel. Glass form was confirmed by XRD (DMAX, Japan).

### *NMR Spectroscopy*

All the NMR experiments were carried out on a DSX 400 Instrument (Bruker Biospin

GmbH, Germany) with a 9.4 Tesla wide-bore magnet at room temperature. Solid state $^{11}B$ NMR spectra were acquired with a CP-MAS probe equipped with 4 mm rotors. Typical sample spinning rate was 13 kHz and its stability was within ± 4 Hz. Solution 90° pulse length for $^{11}B$ was 4 μs and 1 μs pulse length and 20 s repetition delay were used for obtaining $^{11}B$ spectra. Chemical shift was referenced to an external 1 M aqueous $H_3BO_3$ solution.

Spectral simulation was carried out with WINFIT program (Bruker Biospin GmbH, Germany). Powder patterns for central (-1/2-↔1/2) transitions of $^{11}B$ was applied for $BO_3$ sites to get $e^2qQ$ and η while Gaussian/Lorentzian line shapes for $BO_4$ sites with high symmetries.

## RESULTS AND DISCUSSION

In Fig. 1, representative $^{11}B$ MAS NMR spectra of ternary glass system $xV_2O_5$-$B_2O_3$-$yNa_2O$ are shown. $BO_4$ units appear as relatively sharp peaks, on the other hand, $BO_3$ units show powder patterns governed by second order quadrupole interaction. For a binary system without $Na_2O$, $BO_3$ units are observed as a major component as expected from the previous study[6,7] and $e^2qQ$ and η of 2.49 MHz and 0.15, respectively, were obtained from spectral simulation. These values are characteristic of $BO_3$ units in plannar trigonal structures with three bridged oxygens[7,8].

In contrast, in ternary $xV_2O_5$-$B_2O_3$-$yNa_2O$ glasses, in comparable amounts of not only $BO_3$ units but also $BO_4$ units of a tetrahedral shape were detected. Relative populations of $BO_4$ and $BO_3$ units vary as a function of x or y as shown in Fig. 1. Quadrupole parameters as well as relative intensities of $BO_4$ and $BO_3$ units change as a function of x and y as shown in Table 1 and Fig. 2. In general, $e^2qQ$ and η of the ternary samples are a little bigger than those of the binary samples. $e^2qQ$ has a maximum at $x = y = 1$ while η increases and decreases as x and y becomes bigger, respectively. This implies that both $V_2O_5$ and $Na_2O$ start to weaken the gradient strength for $x > 1$ but $V_2O_5$ and $Na_2O$ distorts and improves, respectively, electric field gradient symmetry of $BO_3$ units. At the same time, relative

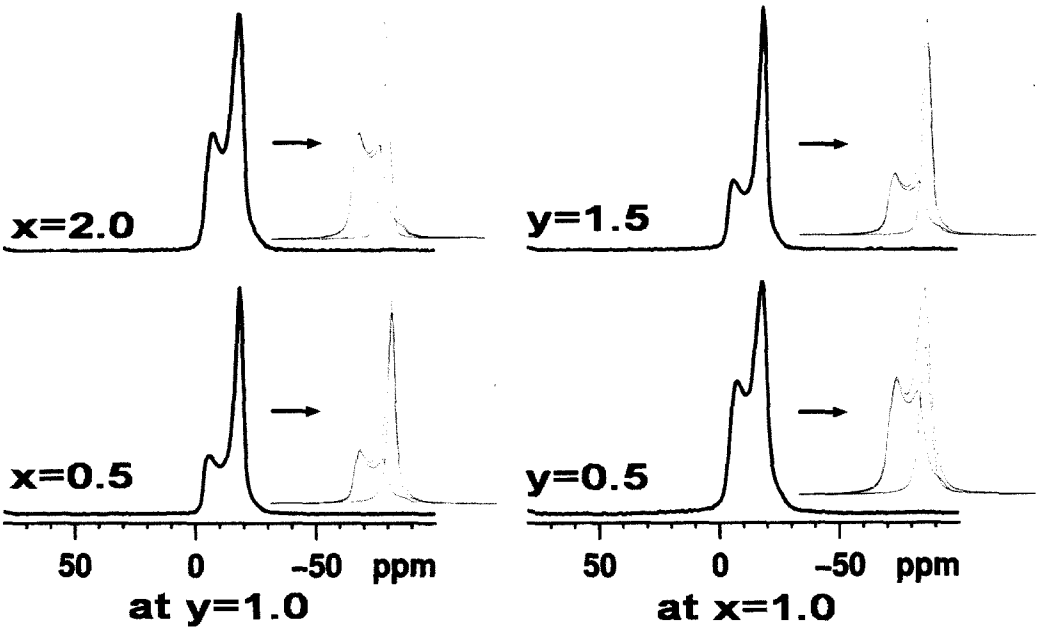


**Fig. 1.** $^{11}B$ MAS NMR spectra of ternary $xV_2O_5$-$B_2O_3$-$yNa_2O$ glasses with various x and y values. Simulation spectra are shown at the right side of each spectrum.

**Table 1.** Summary of sample composition, quadrupole parameters of $BO_3$ unit, relative intensities of $BO_3$ and $BO_4$ units

| $xV_2O_5$-$B_2O_3$-$yNa_2O$ | | Quadrupole Parameters | | Relative Intensity | |
|---|---|---|---|---|---|
| | | $e^2qQ$ (MHz) | $\eta$ | $BO_3$ unit | $BO_4$ unit |
| x = 0.5 | y = 0.5 | 2.55 | 0.20 | 65 | 35 |
| x = 1.0 | | 2.50 | 0.26 | 63 | 37 |
| x = 0.5 | y = 1.0 | 2.56 | 0.17 | 47 | 53 |
| x = 1.0 | | 2.59 | 0.21 | 58 | 42 |
| x = 1.5 | | 2.57 | 0.22 | 63 | 37 |
| x = 2.0 | | 2.55. | 0.22 | 65 | 35 |
| x = 1.0 | y = 1.5 | 2.56 | 0.18 | 50 | 50 |
| x = 1.5 | | 2.50 | 0.11 | 59 | 41 |
| x = 0.05 | y = 0 | 2.49 | 0.15 | $91._8$ | $8._2$ |
| x = 0.42 | | 2.49 | 0.15 | $91._5$ | $8._5$ |

intensities of $BO_4$ units were reduced for higher $V_2O_5$ concentration, which suggests that $V_2O_5$ inhibits transformation of $BO_3$ to $BO_4$ units. Overall bigger $e^2qQ$ values for the ternary glass systems than the binary systems might be simply by more disordering due to more components. In general, relative intensities of $BO_4$ units grow for larger y. This indicates that $V_2O_5$ and $Na_2O$ play opposite roles for relative population variation of $BO_3$ and $BO_4$ units in the glasses.

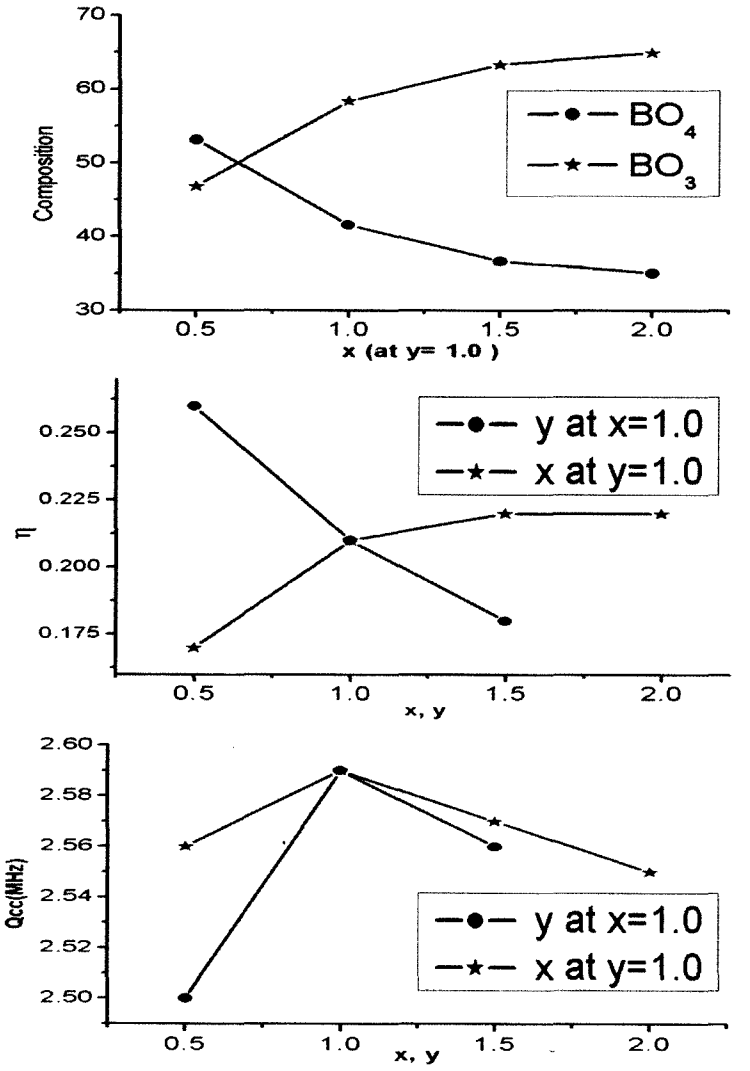


**Fig. 2.** Plots of relative intensities of $BO_3$ and $BO_4$ units, $\eta$, and $e^2qQ$ versus x or y.

In summary, we acquired $^{11}B$ MAS spectra of $xV_2O_5$-$B_2O_3$-$yNa_2O$ glasses with various compositions. By spectrum simulation, relative intensities of $BO_3$ and $BO_4$ units, $e^2qQ$ and $\eta$ for $BO_3$ units were obtained. The glasses without $Na_2O$ have relatively small amounts of $BO_4$ units while comparable amounts of $BO_3$ and $BO_4$ units were observed in the samples with $Na_2O$. In the ternary glasses, more $BO_3$ units are detected for more $V_2O_5$ while more $BO_4$ units for more $Na_2O$. Bigger and smaller $\eta$ values of $BO_3$ units were monitored with lower and higher contents of $V_2O_5$ and $Na_2O$, respectively, while $e^2qQ$ has a maximum value at $x = y = 1$ for both $V_2O_5$ and $Na_2O$ content variations. Thus in general, $V_2O_5$ and $Na_2O$ play opposite roles in the glass systems.

***Acknowledgments***

This work was partially supported by the Korea Research Council of Fundamental Science & Technology through grant PG2313 at KBSI.

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