Solid-state MAS NMR Investigation on the Local Structures of xV_2O_5-B_2O_3-yNa_2O Glasses

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The local structures of the boron and vanadium sites in the ternary glass xV_2O_5-B_2O_3-yNa_2O were studied by ^{11}B and ^{51}V magic angle spinning (MAS) nuclear magnetic resonance (NMR). With increasing x, the mole ratios of the BO_3 and BO_4 structures were enhanced, as were the quadrupole asymmetry parameters for the BO_3 structures, while the quadrupole coupling constants for the sites were reduced. However, the opposite trends were observed with increasing y, implying that V_2O_5 and Na_2O play opposite roles. The VO_4, VO_5 and VO_6 structures with all oxygens bonded to the vanadium neighbors were identified. Vanadiums bonded to the greater number of oxygens were more populated at higher contents of Na_2O and V_2O_5. In addition, the VO_4 structures with at least one oxygen bonded to boron instead of vanadium were detected at low Na_2O contents. The electron densities of various vanadium oxide structures were affected by the weight densities and vanadium ion densities. The VO_4 structures were more likely to be vanadium oxide structures right next to V^{4+} ions.

Key Words: Glass structure, Nuclear magnetic resonance, MAS NMR

Introduction

Although glasses based on V_2O_5 were successfully prepared in the mid 1800s, the semiconducting property of the glasses was reported by Denton *et al.* almost a century later in 1954.[1] Since the conductivity of various vanadate glasses was reported to be due to electrons rather than ionic diffusion,[2] various vanadate glasses have attracted research attention, especially on their conducting properties.[3,4] V_2O_5 does not form a good glass by itself but does form homogeneous glasses with B_2O_3.[1,5] The addition of a small amount of glass network forming oxide to these boro-vanadate glasses was reported to simplify the glass formation.[6] One of the procedures to optimize the properties of mixed glasses has been to change the glass compositions.[1-8] However, the relationships between the local structures and the glass properties have not yet been fully elucidated.

Solid-state nuclear magnetic resonance (NMR) is an excellent spectroscopic methodology to probe the local structures of inorganic materials, especially glasses, since it does not require a sample to have long-range order. Since boron bonded to 3 and 4 oxygens (BO_3 and BO_4 structures, respectively) in alkali borate glasses was identified by ^{11}B NMR by Bray etc.,[8] binary and ternary borate glasses have been studied extensively by ^{11}B NMR and corresponding structural models of the glasses have been reported.[9,10] Likewise, ^{51}V NMR studies on various vanadate glasses have been carried out.[6,11-15] In this work, we identify the local structures of xV_2O_5-B_2O_3-yNa_2O glasses for various levels of x and y using ^{11}B and ^{51}V magic angle spinning (MAS) NMR where x is the mole ratio of V_2O_5 to B_2O_3 and y is the mole ratio of Na_2O to B_2O_3.

Experimental

Sample preparation. Samples were prepared as described in detail in reference.[16] Ternary xV_2O_5-B_2O_3-yNa_2O glasses,

Table 1. ^{11}B MAS NMR spectra simulation results of the xV_2O_5-B_2O_3-yNa_2O glasses

	y	Relative population of BO_3 structure (%)	Relative population of BO_4 structure (%)	Qcc of BO_3 structure (MHz)	η of BO_3 structure
	0.25	87 ± 1	13 ± 1	2.50 ± 0.01	0.28 ± 0.01
	0.5	83 ± 1	17 ± 1	2.52 ± 0.01	0.26 ± 0.01
at x = 2.5	1.0	79 ± 1	21 ± 1	2.53 ± 0.01	0.25 ± 0.01
	1.5	62 ± 1	38 ± 2	2.55 ± 0.01	0.24 ± 0.01
	2.0	61 ± 2	39 ± 2	2.56 ± 0.01	0.21 ± 0.01
	x	Relative population of BO_3 structure (%)	Relative population of BO_4 structure (%)	Qcc of BO_3 structure (MHz)	η of BO_3 structure
	1.0	47 ± 1	53 ± 1	2.60 ± 0.01	0.13 ± 0.01
	1.5	54 ± 1	46 ± 1	2.59 ± 0.01	0.17 ± 0.01
at y = 2.0	2.0	63 ± 1	37 ± 1	2.56 ± 0.01	0.19 ± 0.01
	2.5	61 ± 1	39 ± 1	2.56 ± 0.01	0.21 ± 0.01
	3.0	62 ± 1	38 ± 1	2.55 ± 0.01	0.23 ± 0.01

Table 2. ^{51}V MAS NMR spectra simulation results of the xV_2O_5-B_2O_3-yNa_2O glasses

y	x	Relative population (%)				FWHH (Hz)				Chemical shift (ppm)			
		with V-O-V bonding[a]			with V-O-B bonding[b]	with V-O-V bonding[a]			with V-O-B bonding[b]	with V-O-V bonding[a]			with V-O-B bonding[b]
		VO_4	VO_5	VO_6	VO_4	VO_4	VO_5	VO_6	VO_4	VO_4	VO_5	VO_6	VO_4
0.25	0.25			-	100			-	112			-	-641
	0.5			-	100			-	113			-	-640
	1.5	72	5	-	23	53	20	-	66	-592	-619	-	-655
	2.0	60	21	-	19	58	18	-	55	-599	-620	-	-664
	2.5	54	32	-	14	58	18	-	42	-615	-620	-	-674
	3.0	47	41	-	12	58	18	-	38	-618	-620	-	-675
2.0	1.0	82	18	-	-	46	58	-	-	-564	-587	-	-
	1.5	84	16	-	-	46	66	-	-	-581	-605	-	-
	2.0	84	12	4	-	52	66	46	-	-584	-617	-536	-
	2.5	71	20	9	-	58	76	48	-	-584	-618	-529	-
	3.0	64	24	14	-	66	77	41	-	-584	-622	-520	-

The uncertainty is ± 1 for all the spectral simulation data in the table. [a]The VO_4, VO_5 and VO_6 structures with all oxygens bonded to the vanadium neighbors [b]The VO_4 structures with at least one oxygen bonded to boron instead of vanadium

consisting of a glass network former of B_2O_3, a transition metal oxide of V_2O_5, and an alkaline metal oxide of Na_2O, were produced first by weighing stoichiometric amounts of Na_2CO_3, H_3BO_3, and V_2O_5 (all purchased from Aldrich, U.S.A.) and mixing them well. The mixture was dried in a vacuum oven at 150 °C for about 15 minutes and then transferred to a Pt crucible to melt in an electric furnace (Model 51333 of Lindberg Co., U.S.A.) at 1000 ~ 1100 °C for 30 minutes. A melted mixture was poured onto a smooth stainless steel sheet and covered with another stainless steel sheet to be quenched. Transparent dark brown glasses were produced and the glass quality was checked with an X-ray diffractometer (Model CN2013 of Rigaku, Japan). The nominal mixing mole ratios x and y of the xV_2O_5-B_2O_3-yNa_2O glasses were varied as indicated in Tables 1 and 2.

Sample characterization. The ^{51}V and ^{11}B MAS NMR spectra of the samples were acquired on a Bruker DSX 400 spectrometer with a Larmor frequency of 105.19 and 128.38 MHz, respectively. A spinning speed of 13 kHz with 4 mm zirconia rotors was employed for the ^{11}B MAS NMR spectra while 30 kHz or higher spinning rates with 2.5 mm rotors were required to obtain resolved peaks in the ^{51}V MAS NMR spectra. Pulse repetition delays of 20 s and 1 μs excitation pulses (for a solution 90° pulse of 5 μs) were used for the ^{11}B MAS NMR spectra while pulse repetition delays of 1 s and 0.8 μs excitation pulses (for a solution 90° pulse of 6.4 μs) were used for the ^{51}V MAS NMR spectra. All chemical shifts were referenced against neat $VOCl_3$ liquid, by using saturated $NaVO_3$ aqueous solution (-578 ppm), and against saturated H_3BO_3 aqueous solution for the ^{51}V and ^{11}B spectra, respectively. All the NMR spectrum simulation was carried out with a WINFIT program (Bruker Biospin GmbH, Germany).

Results and Discussion

^{11}B MAS NMR. The ^{11}B MAS NMR spectrum of the xV_2O_5-B_2O_3-yNa_2O glasses consisted of a center band with many spinning side bands. The center band exhibited a powder pattern signal that was broadened by the second-order quadrupole interaction of planar triangle BO_3 structures, as well as a relatively sharp signal from tetrahedral BO_4 structures overlapped with the right shoulder of the powder pattern.[10,16] Figures 1 and 2 show the ^{11}B MAS NMR spectra of the xV_2O_5-B_2O_3-yNa_2O glasses for various y ratios at x = 2.5 and for various x ratios at y = 2.0, respectively. The relative populations of the BO_3 and BO_4 structures, quadrupole parameters (quadrupole coupling constant, Qcc, and quadrupole asymmetry parameter, η) of the BO_3 structures, summarized in Table 1, were obtained from the simulation of the center bands, as shown in the right columns in Figures 1 and 2. The relative populations of the BO_3 structures, as plotted

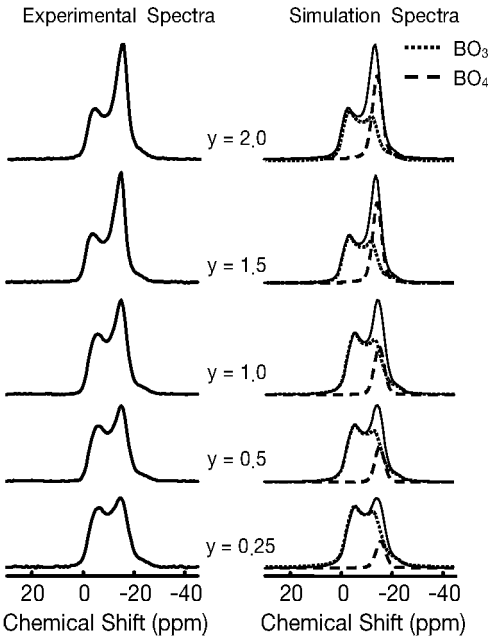

Figure 1. Experimental (left column) and simulated (right column) ^{11}B MAS NMR spectra of the xV_2O_5-B_2O_3-yNa_2O glasses for various y at x = 2.5. The spectra were simulated with the signal contribution from the BO_3 and BO_4 structures.

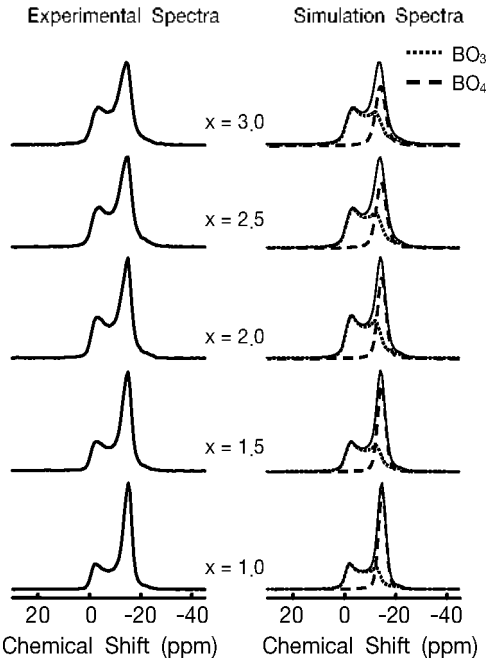

Figure 2. Experimental (left column) and simulated (right column) ^{11}B MAS NMR spectra of the xV_2O_5-B_2O_3-yNa_2O glasses for various x at y = 2.0. The spectra were simulated with the signal contribution from the BO_3 and BO_4 structures.

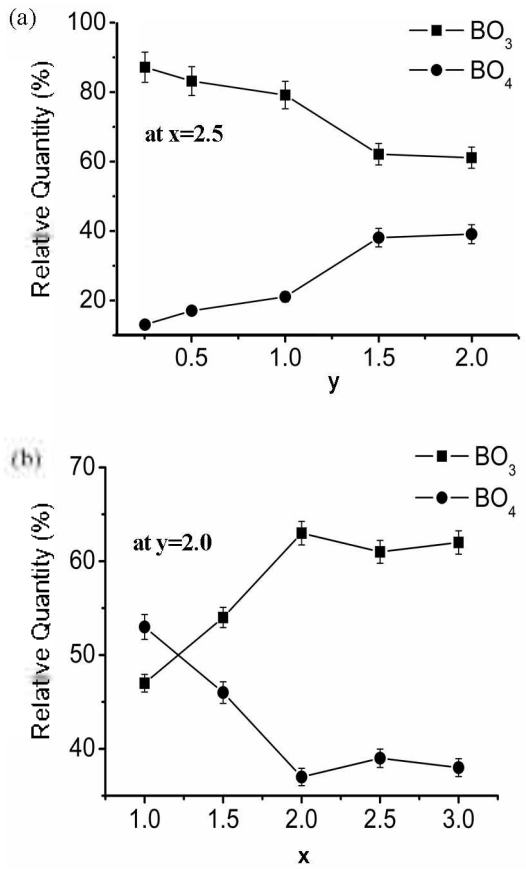

Figure 3. Relative population changes of the BO_3 and BO_4 structures in the xV_2O_5-B_2O_3-yNa_2O glasses for various y at x = 2.5 (a) and for various x at y = 2.0 (b).

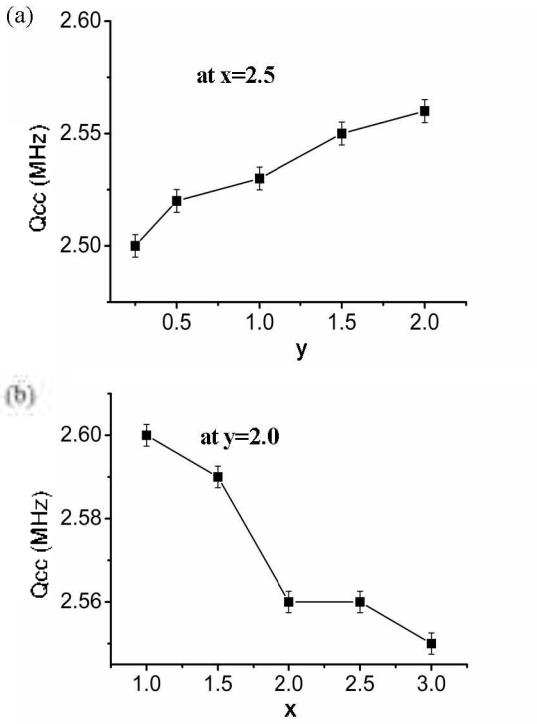

Figure 4. Quadrupole coupling constant (Qcc) changes of the BO_3 structures in the xV_2O_5-B_2O_3-yNa_2O glasses for various y at x = 2.5 (a) and various x at y = 2.0 (b).

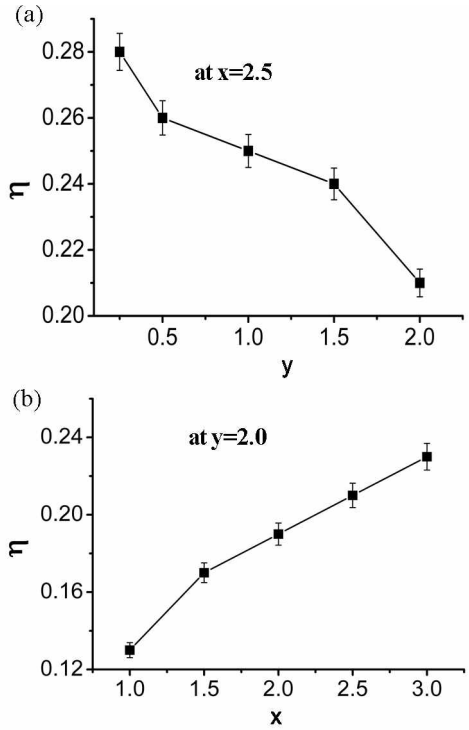

Figure 5. Quadrupole asymmetry parameter (η) changes of the BO_3 structures in the xV_2O_5-B_2O_3-yNa_2O glasses for various y at x = 2.5 (a) and various x at y = 2.0 (b).

in Figure 3, were reduced for increasing y up to 1.5 and then remained constant for larger y while they were increased for increasing x up to 2.0 and then remained constant for larger x. Na_2O apparently converted some of the BO_3 structures into

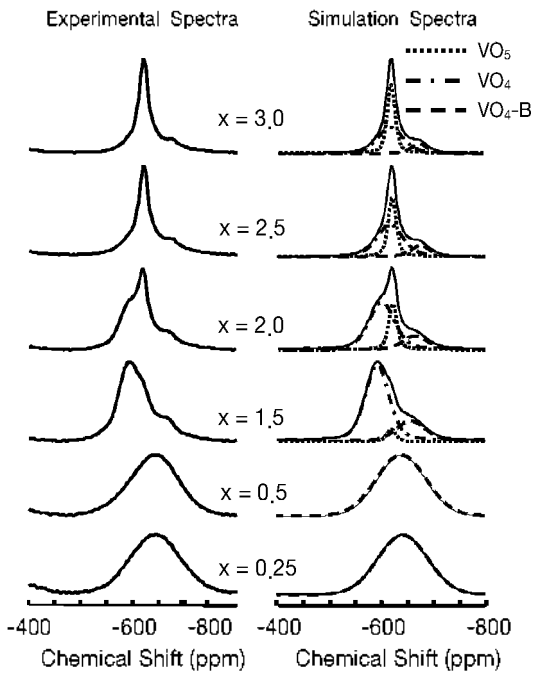

Figure 6. Experimental (left column) and simulated (right column) ^{51}V MAS NMR spectra of the xV_2O_5-B_2O_3-yNa_2O glasses for various x at y = 0.25. The spectra were simulated with the peaks of the VO_4 and VO_5 structures with all oxygens bonded to the vanadium neighbors and of the VO_4 structures with at least one oxygen bonded to boron instead of vanadium (denoted as VO_4-B).

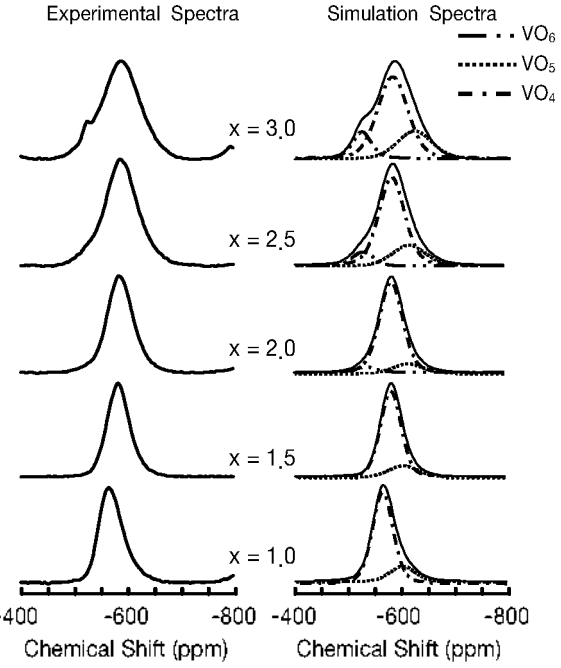

Figure 7. Experimental (left column) and simulated (right column) ^{51}V MAS NMR spectra of the xV_2O_5-B_2O_3-yNa_2O glasses for various x at y = 2.0. The spectra were simulated with the peaks of the VO_4, VO_5, and VO_6 structures with all oxygens bonded to the vanadium neighbors.

BO_4 structures by donating an oxygen atom to the BO_3 structures and by existing as a Na^- ion in the glass up to y = 1.5, as reported previously.[8,17] With higher concentrations of Na_2O in the glass, the Na_2O did not seem to break up anymore. Likewise, the influence of V_2O_5 on the relative populations of the BO_3 and BO_4 structures can be explained as follows: V_2O_5 takes one oxygen atom from the BO_4 structures at x up to 2.0, which thereby increases the relative population of the BO_3 structures. The Qcc value of the BO_3 structures, plotted in Figure 4, increased with increasing y ratio but decreased with increasing x ratio. In contrast, η decreased with increasing y ratio but increased with increasing x ratio, as plotted in Figure 5. These quadrupole parameters indicated (1) that Na_2O increased the electric field gradients at the boron sites of the BO_3 structures but reduced the distortion of the gradients and (2) that V_2O_5 had the opposite effect on the electric field gradients.

^{51}V MAS NMR. The ^{51}V MAS NMR spectrum of the xV_2O_5-B_2O_3-yNa_2O glasses comprised center peaks for each V site and their corresponding spinning side bands. To remove the overlap of the spinning side bands with any center peaks, spinning rates higher than 29 kHz were required at 9.4 T. Four different center peaks, assigned to VO_6, VO_5, and VO_4 structures that were all bonded to neighboring vanadiums and to VO_4 structure with at least one oxygen bonded to boron instead of vanadium,[13,18,19] were obtained from the spectral simulation of the spectra, as shown in Figures 6 and 7. The peaks at −587 ~ −622 ppm were assigned to VO_5 structures as in V_2O_5,[14,15,20] those at −564 ~ −618 ppm to VO_4 structures,[15,21,22] those at −520 ~ −536 ppm to VO_6,[21,22] and those at −640 ~ −675 ppm to VO_4 structures with at least one oxygen bonded to boron instead of vanadium.[13] The relative populations, peak widths, and chemical shifts of the different vanadium oxide structures are summarized in Table 2.

For the xV_2O_5-B_2O_3-yNa_2O glasses of y = 0.25, most of the vanadium sites were present as VO_4 structures with at least one oxygen bonded to boron when y was less than or equal to 0.5, as shown in Figure 2 and Table 2. When x was greater than or equal to 1.5, the population of these VO_4 structures was drastically reduced and VO_5 and VO_4 structures bonded to neighboring vanadiums were detected. At larger x ratios, the VO_5 structures were formed in preference to the VO_4 structures bonded to neighboring vanadiums. Therefore, in the xV_2O_5-B_2O_3-yNa_2O glasses of greater x ratio, the VO_5 structures, i.e., the major structure in V_2O_5, were more produced in the glasses.

In contrast, the VO_4 structures with at least one oxygen bonded to boron were not detected in the xV_2O_5-B_2O_3-yNa_2O glasses with y = 2.0 even at small x ratios while the VO_6 structures, which were not detected at all for y = 0.25, were observed at large x ratios. Thus, higher Na_2O content seemed to have promoted the formation of vanadium sites coordinated with more oxygens and to have simultaneously hindered V-O-B bonding formation. The full width at a half height (FWHH), a measure of the peak width, of the ^{51}V spectra can be influenced by various factors such as the distributions of bond angles and lengths, kinds of the next nearest neighbor atoms, distances to paramagnetic centers such as V^{4+} ions, and quadrupole parameters at the vanadium sites. The Gaussian/Lorentzian peak shapes observed in our ^{51}V spectra indicated that the quadrupolar line broadening is negligible in the center

peaks compared to the other line broadening factors. The vanadium nuclei too close to the paramagnetic centers would not be detected due to the strong dipole interaction with the unpaired electrons. Even when vanadium nuclei located a certain distance away from unpaired electrons are observed, the linewidths are widened in the ^{51}V NMR spectra. If a random distribution and no-mutual-interaction of paramagnetic centers are assumed, the linewidths of all vanadium sites were expected to be influenced similarly. Therefore, the distances to paramagnetic centers such as V^{4+} were unlikely to have been the main cause of the linewidth variations for different vanadium sites observed in the ^{51}V spectra as the glass compositions were varied. At y = 0.25, the most dramatic peak width changes were observed for the VO_4 structures with at least one oxygen bonded to boron. The FWHH was narrowed as more V_2O_5 components were present, as shown in Table 2, which was attributed to binding with fewer B and/ or decreased local structural inhomogeneity with increasing V_2O_5 components in the glass. On the other hand, the FWHH of the VO_5 and VO_4 structures became slightly wider at y = 2.0 with increasing V_2O_5 components, suggesting that the VO_5 and VO_4 structures had wider structural heterogeneities, in the presence of the high Na_2O concentration (y = 2.0), with increasing V_2O_5 concentration. The chemical shifts of the vanadium sites remained constant (for the VO_5 structure at y = 0.25), were downfield shifted (for the VO_6 structure), or upfield shifted (for all the other vanadium oxide structures) with increasing V_2O_5 components, as presented in Table 2.

The refractive indices, conductivities, and densities of the xV_2O_5-B_2O_3-yNa_2O glasses were enhanced in a previous report but the glass transition temperature was lowered with increasing x.[16] In addition, the concentrations of both V^{4+} ions and total vanadium ions in a given volume were also raised, to which was attributed the enhanced conductivities at increasing x.[16] Our chemical shift data suggested that electron densities at each vanadium site were unevenly increased, even when both the weight densities and vanadium ion densities of the xV_2O_5-B_2O_3-yNa_2O glasses were enhanced. V^{4+} ions and vanadium oxide structures next to V^{4+} ions were not detected in the ^{51}V MAS NMR spectra since the dipole interaction with the unpaired electrons of the V^{4+} ions makes the linewidth undetectably wide, especially when a superexchange interaction is present in the V^{4+}-O-V^{5+} chains.[23,24] Thus, the vanadium oxide structures with reduced populations at high V^{4+} ion concentrations, such as the VO_4 structures with at least one oxygen bonded to boron and those bonded to neighboring vanadiums, were more likely to be the vanadium oxide structures right next to V^{4+} ions. However, this was not clearly elucidated in the absence of additional direct evidence to support it.

Conclusions

The local structures of the boron and vanadium sites in the ternary glass system xV_2O_5-B_2O_3-yNa_2O were probed by ^{11}B and ^{51}V MAS NMR. The ^{11}B MAS NMR results confirmed the production of more BO_3 structures than BO_4 structures with increasing x. V_2O_5 and Na_2O were found to play opposite roles in terms of the local structures at the B sites. Our NMR data suggested that Na_2O converted some of the BO_3 structures into BO_4 structures by donating oxygens, induced greater electric field gradients, but reduced the distortion of the electric field gradients at the boron sites of the BO_3 structures. From the ^{51}V spectra, the VO_4, VO_5 and VO_6 structures with all oxygens bonded to the vanadium neighbors were identified, as were the VO_4 structures, with at least one oxygen bonded to boron instead of vanadium, at low Na_2O content of y = 0.25. With increasing Na_2O content in the glass, the vanadium sites coordinated with greater number of oxygens were more populated while less V-O-B bonding was observed. The electron densities at different vanadium oxide structures did not change uniformly with variation in weight densities and vanadium ion densities. The VO_4 structures were more likely to be vanadium oxide structures right next to V^{4+} ions. In future study on this glass system, we aim to clarify the local structure networks by heteronuclear correlation-type NMR experiments and to correlate the functionalities of the glasses with the structure networks.

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