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Site connectivities in sodium aluminoborate glasses: multinuclear and multiple quantum NMR results

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Abstract

In a series of sodium aluminoborate glasses, we have applied triple-quantum magic-angle spinning (3QMAS) ^{17}O NMR to obtain high-resolution information about the connections among various network structural units, to explore the mixing of aluminum and boron species. Oxygen-17 3QMAS spectra reveal changes in connectivites between AlO_4 ($^{[4]}Al$), AlO_5 and AlO_6 ($^{[5,6]}Al$), BO_3 ($^{[3]}B$) and BO_4 ($^{[4]}B$) units, by quantifying populations of bridging oxygens such as Al–O–Al, Al–O–B and B–O–B and of non-bridging oxygens. Several linkages such as $^{[4]}Al$–O–$^{[4]}Al$ and three-coordinated oxygen associated with $^{[5,6]}Al$ in Al–O–Al, $^{[4]}Al$–O–$^{[4]}B$, $^{[4]}Al$–O–$^{[3]}B$ and $^{[5,6]}Al$–O–$^{[3]}B$ in Al–O–B as well as $^{[4]}B$–O–$^{[3]}B$ and $^{[3]}B$–O–$^{[3]}B$ in B–O–B can be distinguished for the first time. The fractions of these linkages were calculated from models of random mixing and of mixing with maximum avoidance of tetrahedral–tetrahedral linkages. The results suggest that the structure of all of glasses in this study is well approximated by the latter model. However, the energetic "penalty" for formation of $^{[4]}Al$–O–$^{[4]}B$ may be somewhat less than for $^{[4]}Al$–O–$^{[4]}Al$ and $^{[4]}B$–O–$^{[4]}B$. In general, the new results presented here are similar to those obtained on glasses in this system by $^{27}Al\{^{11}B\}$ REDOR NMR (J. Phys. Chem. B 104 (2000) 6541), but provide considerably more detail on network connectivity and ordering schemes.

Keywords: Aluminoborate; Glass; ^{17}O; ^{11}B; ^{27}Al; 3QMAS; Aluminum avoidance; Boron avoidance; Tetrahedral–tetrahedral avoidance

1. Introduction

Aluminoborate glasses are of interest in many industrial applications, such as sealing glasses, separators in batteries and dental cement components [1,2]. The degree of mixing among aluminum and boron structural species (i.e., Al/B mixing) is a generally an important issue in controlling and designing physical properties, such as chemical durability, strength at high temperature and crystal nucleation rates. It may also have an important role for both viscosity and diffusivities, which are key properties in batch processing [3,4].

Boron-11 wide-line NMR has long been one of the major tools to study the short-range structure of alkali borate, borosilicate and aluminoborate glasses [5–17]. This work successfully determined the fraction of tetrahedral (BO_4 groups, denoted here as $^{[4]}B$) and trigonal boron species (BO_3 groups, $^{[3]}B$) including symmetric ($^{[3]}B$ connecting three bridging oxygens) and asymmetric trigonal boron groups ($^{[3]}B$ connecting one or two non-bridging oxygens, denoted as $^{[3]}B(1NBO)$ or $^{[3]}B(2NBO)$, respectively). The addition of Na_2O initially results in the change of boron species from symmetric $^{[3]}B$ to $^{[4]}B$ in both binary borate and ternary borosilicate glasses. With increasing Na_2O content in binary borates, the fraction of $^{[4]}B$ among B species (so-called N_4) reaches a maximum and then decreases due to the formation of non-bridging oxygen (NBO) associated with $^{[3]}B$ (asymmetric $^{[3]}B$) [5,8,9]. In borosilicate glasses with increasing Na content, N_4 increases initially, reaches a maximum and then stays constant at a certain

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range of Na_2O content depending on the silicon/boron ratio [10,11]. The addition of Na_2O in this range results in the formation of NBO associated with $^{[4]}$Si. Asymmetric $^{[3]}$B then forms at higher Na_2O content along with the consumption of $^{[4]}$B (decreasing of N_4). Similar to binary borate glasses, N_4 in ternary aluminoborate glasses increases initially and then decreases with the formation of asymmetric $^{[3]}$B with increasing content of modifier oxides [13,15–17].

The role of aluminum oxide in ternary aluminoborate glasses, with alkali or alkaline-earth network modifiers such as calcium, strontium, sodium, potassium and lithium ions, has been studied using ^{11}B and ^{27}Al NMR [13–20]. It has generally been found that Al^{3+} behaves as a network forming cation in such systems. In postulated reaction schemes, the addition of alkali or alkaline-earth oxides to B_2O_3 and Al_2O_3 results in the formation of $^{[4]}$B and $^{[4]}$Al [18,20]. The formation of $^{[4]}$Al and $^{[4]}$B can be considered as competing processes and one can treat the ternary system as a binary system with alkali or alkaline-earth oxide as the modifier and B_2O_3 and Al_2O_3 serving jointly as the network formers. There is preference in the formation of $^{[4]}$Al over that of $^{[4]}$B, since the addition of Al_2O_3 results in a decrease of N_4. The degree of this preference depends on the modifier cation [19].

Aluminum-27 magic angle spinning (MAS) NMR studies on some ternary aluminoborate glasses have found $^{[5]}$Al and $^{[6]}$Al species in addition to $^{[4]}$Al [19–21]. The speciation of Al depends on the composition and the type of modifier cation. In general, high coordinated Al species, i.e., $^{[5]}$Al and $^{[6]}$Al, become significant when the molar ratio of modifier cation to Al is smaller than one. $^{[4]}$Al is usually predominant in sodium aluminoborate glasses [19,20], while large fractions of $^{[5]}$Al and $^{[6]}$Al species are seen in the presence of highly polarizing cations, such as Mg^{2+} and Ca^{2+} [19,21].

The stability of various oxygen species associated with different Al and B species has been evaluated based on local charge balance considerations [22]. It was proposed that $^{[5]}$Al and $^{[6]}$Al could be associated with oxygens with higher coordination numbers (3 or 4; not counting modifier cations). It was also predicted that modifier cations with higher ionic potential promote the stability of higher coordination numbers on both network forming cations and oxygen anions, as has also been seen in aluminosilicates [23]. In addition, the relatively highly charged $^{[4]}$B–O–$^{[4]}$B and $^{[4]}$Al–O–$^{[4]}$Al oxygens were suggested to be less stable than $^{[3]}$B–O–$^{[4]}$Al.

Double resonance NMR techniques, such as ^{11}B{^{27}Al} and ^{27}Al{^{11}B} rotational echo double resonance (REDOR) and cross-polarization (CP) MAS, have been applied to sodium-, calcium- and magnesium aluminoborate glasses to probe the connectivities between B and Al species [18,19,24,25]. In general, these studies have shown that $^{[4]}$Al species connect preferentially to $^{[3]}$B over $^{[4]}$B species and that $^{[4]}$B is more likely to interact with $^{[5]}$Al and $^{[6]}$Al rather than $^{[4]}$Al. The $^{[4]}$Al–$^{[4]}$B interactions (or, in general, links between trivalent, tetrahedral network cations) are disfavored to an extent that is highly dependent on the framework composition and on the type of modifier cation. Sodium aluminoborate glasses reveal a strong chemical ordering (avoidance of inter-tetrahedral linkages), whereas the analogous magnesium-based glasses tend to mix randomly [19]. In glasses with low Al and/or high modifier contents, there may be a greater tendency toward a random mixing [18].

Oxygen-17 NMR can provide more direct information about connectivities among various cations. However, conventional MAS spectra can be limited by the poor resolution due to the second-order quadrupolar broadening. The triple quantum magic angle spinning (3QMAS) technique [26,27] was developed to eliminate such broadening, by providing two-dimensional (2-D) spectra with one-dimension free of such broadening. The greatly improved resolution provided by ^{17}O 3QMAS technique has allowed resolution of various types of bridging oxygen sites such as Si–O–Si, Si–O–B, B–O–B, B–O–Al, Si–O–Al and Al–O–Al as well as NBOs in binary borosilicate and aluminosilicate glasses and ternary borosilicate and aluminoborate glasses [28–38].

In our recent studies of alkali borosilicate glasses [28–30], we showed that even more detailed structural units can be found in 3QMAS spectra, including $^{[3]}$B(ring), $^{[3]}$B(non-ring), $^{[4]}$B(iB,(4−i)Si) for $i = 0$, 1, 2 in ^{11}B data and NBO, Si–O–Si, Si–O–$^{[4]}$B, Si–O–$^{[3]}$B, $^{[4]}$B–O–$^{[3]}$B, and $^{[3]}$B–O–$^{[3]}$B in ^{17}O data. This provides a greatly increased amount of information to explore issues such as the effects of alkali type and content, of Si/B ratio, and of annealing on the glass structure. Furthermore, the extent of mixing with Si for each B species can be differentiated and quantified based on the mean numbers of Si neighbors to boron units obtained by the combination of ^{17}O and ^{11}B NMR data.

In our study of sodium aluminoborate glasses presented here, several samples, with a number of Al/B and Na/B ratios, were made and examined by ^{11}B, ^{27}Al and ^{17}O NMR. From the high field ^{11}B and ^{27}Al MAS NMR data collected at 14.1 and 18.8 Tesla (T), the populations of boron and aluminum species can be obtained. The populations of a variety of oxygen species can be obtained from the high resolution provided by ^{17}O 3QMAS NMR at 14.1 T. The experimental data are then compared with the populations of oxygen species calculated from different models, such as statistical random mixing or mixing considering the avoidance of $^{[4]}$M–O–$^{[4]}$N (M, N = Al or B), in order to begin to explore the mixing behavior between $^{[4]}$B, $^{[3]}$B, $^{[4]}$Al and $^{[5,6]}$Al species.