



Non-stoichiometric non-bridging oxygens and five-coordinated aluminum in alkaline earth aluminosilicate glasses: Effect of modifier cation size

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ABSTRACT

Both non-bridging oxygen (NBO) and high-coordinated aluminum (commonly ^VAl at atmospheric pressure) are believed to play important roles in the thermodynamic and transport properties of aluminosilicate melts but their changes with composition are not well understood, particularly in compositions that are charge-balanced or contain excess alumina. Here we present high-resolution ^{27}Al and ^{17}O MAS NMR data on barium aluminosilicate glasses, similar to previously studied calcium and potassium aluminosilicate glasses, allowing us to separate the effect of cation size versus cation charge. The NBO content decreases with increasing Al content but shows no significant difference compared to similar calcium aluminosilicate glasses. As there is a significant difference between similar potassium and calcium aluminosilicate glasses, this indicates that cation charge may be the important parameter in determining the amount of NBO present on the charge-balanced join. The ^VAl content increases with increasing Al content but is significantly lower than similar calcium aluminosilicate glasses. This data, together with the data from potassium and calcium aluminosilicate glasses, agrees with the well-known effect of increasing high coordinated aluminum with higher cation field. In contrast, the lack of changes observed in the “non-stoichiometric” NBO content despite the changes in the ^VAl content provides additional evidence to suggest that the formation of NBO and ^VAl is not linked.

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1. Introduction

The relationship between the atomic scale structure of aluminosilicates and their macroscopic and thermodynamic properties remains the subject of much research, owing to their importance in both geological processes and technology. At this point, it is understood that the structure of silicate glasses and melts impacts such properties as viscosity, silica activity, diffusivity, and density [1–3]. Of particular interest is the proportion of non-bridging oxygen (NBO, an O atom bound to a single network former and requiring network modifiers to balance the remaining valence charge), which has a significant impact on the hardness, chemical durability, and glass transition temperature of a given glass, as well as impacting thermodynamic and transport properties [4,5]. The amount of NBO present in a glass is often given as a percentage of the total oxygen or as the mean number of NBO per cation in tetrahedral coordination (NBO/T).

It is common to see the NBO content in glasses deduced from the glass composition alone, which requires several assumptions about glass structure. The most commonly used model, referred to here as the “standard” model, begins with concepts derived from known crystal structures and assumes that in ambient pressure melts with

modifier oxides equal to or in excess of the alumina content (e.g., $\text{mol}\% \text{Al}_2\text{O}_3 \leq \text{BaO}$ or K_2O), all Al^{3+} cations are four coordinated. At the metaluminous join, where the alumina and modifier oxides are balanced (e.g., $\text{mol}\% \text{Al}_2\text{O}_3 = \text{BaO}$ or K_2O), the general assumption is that all O atoms are bridging (BO); subsequent additions of modifier oxide result in increased NBO. The NBO content in these melts is assumed to follow the stoichiometric reaction, with 2 moles of NBO formed for each “excess” mole of modifier oxide. The “standard” model offers no guidance regarding structural behavior in peraluminous regions (e.g., $\text{mol}\% \text{Al}_2\text{O}_3 > \text{BaO}$ or K_2O).

Research into glass structure has forced a revision of this “standard” model, beginning with evidence from possible nonlinear effects of composition on melt density and viscosity [6,7] and viscosity peaks offset from their expected maxima at the metaluminous join [8,9]. Direct observation of non-stoichiometric species (i.e. not predicted by standard models) such as NBO on the metaluminous join [10,11] or ^VAl in the modifier-rich compositions, primarily in calcium aluminosilicates [12,13] and also in magnesium and alkali aluminosilicates [14–17], has come from high-resolution NMR studies. High-coordinated aluminum is also predicted in significant quantities by some molecular dynamics simulations of aluminosilicates, although this depends on model potentials and represents the melt at very high temperature [18–21]. Most non-tetrahedral aluminum has been found in five-fold coordination; even in the peraluminous region, recent work has found substantial quantities of ^VAl with only small amounts of ^VAl in the most peraluminous glasses [12].

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Much of this research has made clear that changes due to composition must be better understood before it will be possible to construct a more accurate model of glass or melt structure, particularly in regions close to the metaluminous join where deviations from the “standard” model are the greatest. Despite finding between 4 and 7% of the total Al as ^VAl in a significant portion of the calcium-rich region of the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ phase diagram, there are still areas with high silica content or low-silica and high-calcia content that do not have any ^VAl within the limit of detection, estimated at approximately 0.5% of the total Al content [22]. The rate of change in ^VAl content with composition in the peraluminous region has also been shown to offer potential insights into the structural mechanisms for incorporating “excess” alumina (above the amount the modifier cations can charge balance) into the melt and the roles that ^VAl play [11]. However, important questions still remain, particularly regarding potential linkages between NBO and ^VAl content in the metaluminous and peraluminous regions. One parameter of interest is the field strength of the modifier cation, defined as the cation charge divided by the square of the cation–oxygen ionic bond distance. Cation field strength has been found to play a large role on the percentage of aluminum present as ^VAl in high-pressure melts [14,23] and rare-earth aluminosilicate glasses and melts [24,25] and may offer insight into a potential relationship between NBO and high-coordinated aluminum.

In this study, we present experimental data on the effect of composition on the NBO and ^VAl content in a series of barium aluminosilicate (BaAS) glasses crossing the metaluminous join. The BaAS system was chosen because the ^{17}O MAS NMR peaks for the NBO and BO are well resolved due to the impact of chemical shift effects on isotropic chemical shift, δ_{iso} , similar to that observed in the potassium and calcium systems and as noted in a previous study of Ba borosilicates [26]. Additionally, the barium cation has the same charge as calcium but is larger, giving it a field strength between the previously studied cations (calcium and potassium [11]) and allowing us to separate the effects of cation charge and size (see Table 1). These data are then compared to existing data for a series of calcium aluminosilicate glasses of similar composition [11] to examine the impacts of cation field strength on NBO content and ^VAl content. Finally, the relationship between changes in the NBO and ^VAl contents is also examined to investigate the possibility of a mechanism linking the formation of NBO and ^VAl in the region near the metaluminous join.

2. Experimental

The barium aluminosilicate glasses were prepared from reagent-grade Al_2O_3 , BaCO_3 , and 45% ^{17}O -enriched SiO_2 , dried overnight at 250 °C and then ground together to produce approximately 100 mg of sample. In order to speed spin–lattice relaxation and permit faster NMR data collection, Co_3O_4 was added to the sample at 0.2 wt.%. The starting mixtures were decarbonated and then melted under Ar in Pt crucibles at 1690 °C for 2 h and quenched by dipping the bottom of the crucible in water. Samples are labeled here by their nominal composition, per our previous study, noted here as BaASx.y.z, where x is the mol% of BaO , y is the mol% of Al_2O_3 , and z is the mol% of SiO_2 . No crystals were detected using optical microscopy. Sample compositions were checked by electron microprobe analysis, with the results

Table 1
Calculated cation field strengths of calcium, barium, and potassium.

Modifier cation	Cation radius (\AA) ^a	Cation field strength (Z/D^2) ^a
Ca^{2+}	1.00	0.36
Ba^{2+}	1.42	0.26
K^+	1.51	0.12

^a Cation radius and field strength values from Brown et al. [52].

given in Table 2. As in our previous study [11], the R value represents the ratio of modifier oxide to the modifier oxide plus alumina (e.g., $R = \text{BaO}/(\text{BaO} + \text{Al}_2\text{O}_3)$) and is calculated using the electron microprobe analyses of the glasses. The analyzed compositions were used for all data plots and interpretations. Where possible, compositions were matched to the previously studied CAS and KAS compositions; however, the higher melting temperatures required restricted the range of available BaAS compositions to the 30 mol% SiO_2 isopleth.

For both ^{27}Al and ^{17}O , the 1D MAS NMR spectra were collected at room temperature with Varian Unity/Inova spectrometers at 18.8 and 14.1 T fields, using Varian/Chemagnetics “T3” probes with 3.2 mm zirconia rotors spinning at 20 kHz, referenced to either aqueous $\text{Al}(\text{NO}_3)_3$ or ^{17}O -enriched H_2O . Spectra were acquired using a single pulse excitation with pulse widths of about 0.2 μs (for ^{27}Al) or 0.3 μs (for ^{17}O), corresponding to about 30° radio frequency tip angles in the solid. Delays of 0.1 s (for ^{27}Al) and 1 s (for ^{17}O) were used between pulses to optimize the signal-to-noise ratio. Checks for differential relaxation times for different sites yielded no differences in signal, and plotted spectra are normalized to the highest peak maxima. Quantification of both oxygen and aluminum speciation was done using the software package Dmfit, using the same technique described in the previous study on similar samples to allow for comparison [11,27].

3. Results

3.1. Oxygen

The ^{17}O MAS NMR spectra (Fig. 1) for all the glasses studied here exhibit a large, asymmetric peak centered near 80 ppm attributed to the bridging oxygens (including Si–O–Al, Si–O–Si, and Al–O–Al) and accompanied by a second, smaller peak to the high-frequency (left-hand) side. This smaller peak is uniquely assignable to NBO based on data from crystalline compounds and binary barium silicate glasses [28,29]. Both the NBO and BO peaks observed here are broader than their counterparts in calcium aluminosilicate glasses, as seen in Fig. 2. Triclusters, or oxygen bonded to three tetrahedral aluminum or silicon, have also been suggested to explain deviations from the “standard” model [9]. Data from quantum calculations and NMR studies in the calcium system indicate that if triclusters are present, their ^{17}O NMR peak is likely overlapped by the large BO peak [30–32]. However, if any triclusters are present, this overlap has no impact on the experimental determination of NBO as a percentage of total oxygen.

For the barium aluminosilicate glasses, the NBO peak area decreases as the glass becomes more peraluminous (that is, the R value decreases). It does not decrease below the limit of detection (estimated to be <0.5% of the total oxygen content) in any of the glasses studied here. The results of the quantitative fits are shown in Table 3, with the uncertainties estimated to be approximately $\pm 0.7\%$. A simple linear fit can be used as a rough first approximation to estimate the “disappearance” point of the NBO as a function of R value in this series; it occurs at $R = 0.42$, as shown in Fig. 3.

Table 2
Analyzed compositions of BaASx.y.30 glasses.

Sample name	mol% BaO^a	mol% Al_2O_3^a	mol% SiO_2^a	R^b
BaAS38.32.30	35.7	33.7	30.6	0.51
BaAS35.35.30	34.8	36.0	29.2	0.49
BaAS32.38.30	34.0	38.1	28.0	0.47
BaAS30.40.30	32.9	39.8	27.3	0.45

^a Analyses from electron microprobe. Error range estimated at ± 0.5 mol%.

^b Error estimated at ± 0.01 .

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