Cation Distribution in Mixed Alkali Disilicate Glasses

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Abstract: We have investigated the structure of five disilicate glass compositions—K2O·2SiO2, (Na0.25K0.75)2O·2SiO2, (Na0.50K0.50)2O·2SiO2, (Na0.75K0.25)2O·2SiO2, and Na2O·2SiO2—using 2D 17O Dynamic Angle Spinning (DAS) Nuclear Magnetic Resonance (NMR). The nonbridging and bridging oxygen sites can be resolved in the isotropic 17O DAS spectrum. The bridging oxygen isotropic resonance shifts from 16.1 ppm in K2O·2SiO2 to 11.8 ppm in Na2O·2SiO2 and remains almost identical in width. The nonbridging oxygen isotropic line shapes in the mixed compositions are broader with a maximum intensity that continuously shifts from the position found in the pure potassium composition to the position found in the pure sodium composition. The evolution of the nonbridging oxygen isotropic line shape with changing alkali composition is consistent with a model of the glass structure where four alkali cations are distributed in random combinations around each nonbridging oxygen.

Introduction

The recent advent of solid-state NMR techniques, like Dynamic-Angle Spinning (DAS)1–7 which provide high resolution solid-state NMR spectra of quadrupolar nuclei, is giving new insight into the structure of glasses.8–11 One of the areas where this technique can provide a fresh view of an old problem is the mixed alkali effect. In the “mixed alkali effect” a linear addition in alkali ions of a second type into a single alkali silicate is the mixed alkali effect. In the “mixed alkali effect” a linear addition in alkali ions of a second type into a single alkali silicate glass changes by an order of magnitude the electrical conductivity and the viscosity of the glass in a nonlinear fashion.12 At present, there is considerable debate over the mechanism for this effect. Current theories of the “mixed alkali effect” in glasses rely heavily upon various models of the glass structure.13,14 The Modified Random Network model15,16 postulates the existence of nanoscaled zones composed of pure ν-SiO2 surrounded by alkali channels. The Cluster Bypass model17 describes the glass structure as a network of microdomains (with a size of ≈5 nm) connected by a “tissue” of a different compositions. The Mixed-Alkali Defect model18 relies on the existence of dedicated cation sites into which foreign cations can be locked. Since few experiments are available for investigating topological order and disorder in glasses, no particular model has yet been completely confirmed from experimental techniques.

The ternary system Na2O—K2O—SiO2 is known to exhibit all the characteristics of the “mixed alkali effect”12 and has been studied by scattering19,20 and computational techniques.21,22 In this paper we investigate this model system using 17O DAS NMR. This nucleus can monitor the short range structure modifications in those alkali disilicate glasses as the composition changes from one single alkali to another. The nonbridging oxygen sees most if not all of the two types of network modifying cations and thus provides valuable information about their distribution in the glass. Related changes in the SiO4 network can be directly monitored through the position and width of the bridging oxygen resonances.

Experimental Section

Sample Preparation and Characterization. The five glass compositions synthesized were K2O·2SiO2, (Na0.25K0.75)2O·2SiO2, (Na0.50K0.50)2O·2SiO2, (Na0.75K0.25)2O·2SiO2, and Na2O·2SiO2.

since its bonding is more ionic than the bridging oxygen. The quadrupolar broadenings, is smaller for the nonbridging oxygen peak while changing the composition: the bridging oxygen peak remains almost unchanged in position and the nonbridging peak moves to lower frequency (higher shielding) by about 3 ppm. This assignment is further confirmed by the evolution of each group II oxides have been shown to increase with the cation ionic radius (Ahrens ionic radii: 0.97 Å for Na and 1.33 Å for K), with a more marked dependence for the nonbridging oxygen peak. The observed isotropic position  will be further denoted as \( \delta^{iso} \) and \( \delta^{iso} \) are clearly resolved in the two-dimensional spectrum of the 17O DAS spectra for all five compositions are shown in Figure 1, and was shifted by an integer number of rotor periods. The two-dimensional \( \delta^{iso} \) relaxations times were estimated using saturation recovery experiments under MAS conditions and assuming a single exponential recovery as first approximation. No differences in the 17O chemical shifts in alkaline-earth metasilicates and in 

**Discussion**

The resonances for the bridging and nonbridging oxygens are clearly resolved in the two-dimensional spectrum of \( \nu_2 \)-K\(_{50}\)Na\(_{50}\) shown in Figure 1. As expected, the width in the anisotropic dimension, which is dominated by second-order quadrupolar broadenings, is smaller for the nonbridging oxygen since its bonding is more ionic than the bridging oxygen. This assignment is further confirmed by the evolution of each peak while changing the composition: the bridging oxygen peak remains almost unchanged in position and the nonbridging oxygen peak moves to lower frequency (higher shielding) by addition of sodium in the glass. This behavior is expected since the 17O chemical shifts in alkaline-earth metasilicates and in the group II oxides have been shown to increase with the cation ionic radius (Ahrens ionic radii: 0.97 Å for Na and 1.33 Å for K), with a more marked dependence for the nonbridging oxygen than for the bridging oxygen.

The observed isotropic position \( \delta^{obs} \) is defined by:

\[
\delta^{obs} = \delta^{CS} + \delta^{2Q}^{iso}
\]

(1)

where \( \delta^{CS} \) is the isotropic chemical shift and \( \delta^{2Q} \) is the second-order quadrupolar isotropic shift, both expressed in ppm. For a spin I with a Larmor frequency \( \nu_I \), a nuclear quadrupole coupling constant \( C_Q \) and a quadrupolar asymmetry parameter \( \eta \), \( \delta^{2Q} \) is defined by:

\[
\delta^{2Q}^{iso} (ppm) = - \frac{3}{40} \left( \frac{C_Q}{\nu_I} \right)^2 \frac{I(I+1) - 3/4}{I^2(2I-1)^2} \left( 1 + \frac{\eta^2}{3} \right) \times 10^6 \]

(2)

The observed position is therefore a function of both the isotropic chemical shift and the quadrupolar parameters. There is very little variation of the bridging oxygen isotropic line shape with changes in composition. In addition, the mean isotropic shift varies from 16.1 to 11.8 ppm in going from the potassium to the sodium composition. This may be an effect of the alkali cations, and/or changes in the Si–O–Si bond angle distribution, and/or ring size distribution. Significant variations in the bridging oxygen isotropic lineshape across the isotropic line shape can be seen for each composition. As previously shown, these variations are attributed to a continuous distribution in \( C_Q \) and \( \eta \) for the bridging oxygens. These distributions can be correlated to changes in Si–O–Si bond angle and in principle, can be used to map the isotropic line shape of the bridging oxygen into the Si–O–Si bond angle distribution for these glasses. Unfortunately, the detection angle used in these experiments hinders this analysis due to the probable presence of chemical shift anisotropy that complicates the line shape fitting procedure. Ignoring the chemical shift anisotropy and fitting for quadrupolar anisotropy alone

would lead to inflated quadrupolar coupling constants and be interpreted as larger Si–O–Si angles. To eliminate the interference from chemical shift anisotropy and obtain accurate quadrupolar coupling parameters for the bridging oxygens magic-angle-spinning detected DAS would be required.

For all compositions the anisotropic line shapes of the nonbridging oxygen sites are constant as a function of isotropic dimension for the nonbridging oxygen is dominated by isotropic chemical shift dispersion.

The influence of the alkali cation on the nonbridging oxygen peak position is clearly seen in the five isotropic projections shown in Figure 2. Although there is a progressive overlap of the bridging and nonbridging oxygen peaks as the sodium content increases, it is still possible to deconvolute each of the five spectra into two components. Table 2 summarizes the “best” fits results assuming a mixture of Gaussian and Lorentzian line shapes. In all cases, the ratio of the integrated areas for the bridging and nonbridging oxygens falls reasonably close the 60/40 expected ratio for a disilicate composition.

Typical nonbridging oxygen isotropic line widths in the crystalline state are on the order of 200 Hz. For both the pure sodium and potassium compositions, the line width is ≈900 Hz, indicating that the disorder around the nonbridging oxygen is of the same extent for both compositions. This width results from the disorder around the nonbridging oxygen sites which produces a distribution in isotropic chemical shifts. Since there is a unique type of alkali cation present in those two glasses, the observed broadening reflects a disorder in the length and orientation of the alkali cation–nonbridging oxygen internuclear vector. This can be related to the spread of cation-oxygen distances $R_{M-O}$ (and therefore oxygen–cation distance $R_{O-M}$) of $\approx \pm 0.5$ Å observed by EXAFS in sodium, potassium, and cesium disilicate glasses.

The nonbridging oxygen line shapes in the mixed compositions are almost twice as large as those in the pure glasses. To understand this behavior we assume that the nonbridging oxygen is 5-fold coordinated in the five glasses under study, i.e., the nonbridging oxygen is coordinated by 1 silicon and 4 alkalis. This assumption is supported by EXAFS studies of several alkali silicates that led to the idea that the nonbridging oxygen coordination number lies between 4 and 6, closely matching the alkali coordination number. Related studies as well as Molecular Dynamic calculations have also shown that the coordination number of sodium in $\nu$-K$_{100}$Na$_{40}$ is $5 \pm 0.5$. In addition, a later study suggested that the cation coordination number is not changed by addition of potassium, and that strong similarities in the structure of the cation and the nonbridging oxygen clusters has been found between sodium and potassium disilicate glasses. Therefore, with this fixed coordination number, only a limited number of nonbridging oxygen types can be created in the mixed composition: Si–O–Na$_4$, Si–O–Na$_3$K, Si–O–Na$_3$K$_2$, Si–O–Na$_3$K$_3$, Si–O–Na$_3$K$_4$, and Si–O–K$_4$.

Table 2. Results of the Fit of the Isotropic Projection of the 2D $^{17}$O DAS Spectra of (a) $\nu$-K$_{100}$Na$_{60}$, (b) $\nu$-K$_{75}$Na$_{25}$, (c) $\nu$-K$_{60}$Na$_{40}$, (d) $\nu$-K$_{50}$Na$_{50}$, and (e) $\nu$-K$_{25}$Na$_{75}$

<table>
<thead>
<tr>
<th>composition</th>
<th>$\Delta v_{BO}$ (ppm)</th>
<th>$\Delta v_{NBO}$ (ppm)</th>
<th>$\Delta v_{BO}$ (Hz)</th>
<th>$\Delta v_{NBO}$ (Hz)</th>
<th>$G/L_{BO}$</th>
<th>$G/L_{NBO}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$-K$<em>{100}$Na$</em>{60}$</td>
<td>16.1 1276 1.0</td>
<td>68.7 937 1.0</td>
<td>55/45</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$\nu$-K$<em>{75}$Na$</em>{25}$</td>
<td>16.3 1336 0.8</td>
<td>58.9 1563 1.0</td>
<td>62/38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu$-K$<em>{60}$Na$</em>{40}$</td>
<td>15.6 1579 0.7</td>
<td>46.4 1592 0.3</td>
<td>62/38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu$-K$<em>{50}$Na$</em>{50}$</td>
<td>12.5 1414 0.9</td>
<td>31.0 1676 0.8</td>
<td>59/41</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\nu$-K$<em>{25}$Na$</em>{75}$</td>
<td>11.8 1207 0.6</td>
<td>27.0 839 0.6</td>
<td>56/44</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\delta$ is the position of the maximum, $\Delta v$ is the full width at half maximum, $x = G/L$ refers to the $x \times$ Gaussian + $(1-x) \times$ Lorentzian shape, and BO/NBO is the calculated ratio of bridging over nonbridging.

Table 1. Experimental Conditions Used for the DAS Experiments

<table>
<thead>
<tr>
<th>composition</th>
<th>rec delay</th>
<th>$T_{1}$ at 37 °C (µs)</th>
<th>$T_{2}$ at 79 °C (µs)</th>
<th>dwell times (µs)</th>
<th>no. of scans</th>
<th>$t_{1} \times t_{2}$</th>
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</thead>
<tbody>
<tr>
<td>$\nu$-Na$<em>{4}$K$</em>{100}$</td>
<td>0.3 0.4</td>
<td>22.5 14.0</td>
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<td>1024</td>
<td>30 × 256</td>
<td></td>
</tr>
<tr>
<td>$\nu$-Na$<em>{2}$K$</em>{75}$</td>
<td>3.0 5.0</td>
<td>15.0 15.0</td>
<td>40</td>
<td>2048</td>
<td>32 × 256</td>
<td></td>
</tr>
<tr>
<td>$\nu$-Na$<em>{50}$K$</em>{50}$</td>
<td>1.8 3.0</td>
<td>22.5 14.0</td>
<td>40</td>
<td>4096</td>
<td>38 × 256</td>
<td></td>
</tr>
<tr>
<td>$\nu$-Na$<em>{5}$K$</em>{25}$</td>
<td>2.5 3.0</td>
<td>15.0 15.0</td>
<td>40</td>
<td>4096</td>
<td>32 × 256</td>
<td></td>
</tr>
<tr>
<td>$\nu$-Na$<em>{10}$K$</em>{100}$</td>
<td>0.4 0.5</td>
<td>22.5 14.0</td>
<td>40</td>
<td>4096</td>
<td>71 × 256</td>
<td></td>
</tr>
</tbody>
</table>


to the spectrum of the mixed glasses. To be consistent with the known line shapes observed for Si–O–Na\textsubscript{a} (\textit{v}-K\textsubscript{100} Na\textsubscript{0}) and Si–O–K\textsubscript{a} (\textit{v}-K\textsubscript{100} Na\textsubscript{0}) we can assume that those characteristic contributions will be of a Gaussian/Lorentzian type with a line width of \(\sim 900\) Hz. This should take into account the cation–oxygen distance disorder, assuming it to be constant across all compositions. The non-observation of two resolved peaks for the nonbridging oxygen precludes a structural model with only two types of nonbridging oxygen sites (e.g., if significant clustering of alkali is occurring). If only two sites existed then the two 900 Hz wide peaks must have a separation of \(\sim 700\) Hz (\(\sim 13\) ppm) in order to reproduce the \(\sim 1600\) Hz observed line widths. This separation, however, would lead to a mixed glass spectrum that exhibits two maxima for the nonbridging oxygen site which is clearly not observed for the \(v\)-K\textsubscript{50}Na\textsubscript{50} and \(v\)-K\textsubscript{25}Na\textsubscript{75} compositions. One could also argue that the data are consistent with only one type of nonbridging oxygen existing in the mixed glasses and that as a result of the cation–oxygen distance disorder this nonbridging oxygen line width is increased when both compositions are mixed together. This argument, however, is not justified by EXAFS data\textsuperscript{30} which show that the greatest cation–oxygen distance disorder in mixed alkali disilicate glasses is in the pure alkali composition of the alkali cation with the smallest radius, not the mixed alkali composition.

A structural model that is consistent with our results is the ideal solution model,\textsuperscript{32} where the different alkali cations are distributed in random combinations around each nonbridging oxygen and it is assumed there is no energy change associated with a rearrangement of the K and Na cations. If this were the case we would expect the populations of the five different nonbridging oxygen environments to be dictated by the binomial distribution. According to the binomial distribution, the number of sites in which an environment Si–O(Na\textsubscript{a}K\textsubscript{4}) where \(k = 0, \ldots, 4\) occurs in a glass of alkali composition (Na\textsubscript{\textit{p}}K\textsubscript{1–\textit{p}})\textsubscript{2}SiO\textsubscript{2} (\(0 \leq p \leq 1\)) will be given by:

\[
P(k) = \frac{4!}{k!(4-k)!} p^k (1-p)^{4-k}
\]  

(3)

To test this model we simultaneously fit all five isotropic spectra in Figure 2 with the constraints that the relative intensity of each Si–O(Na\textsubscript{a}K\textsubscript{4}) component composing the nonbridging oxygen line shape follows the binomial distribution values dictated by the composition. Therefore, the simultaneous fit parameters describing all the nonbridging oxygen line shapes are the five positions and five widths of each Si–O(Na\textsubscript{a}K\textsubscript{4}) component, assuming that all components share the same Gaussian/Lorentzian line shape ratio. In addition, the bridging oxygen line shapes were all fit with the constraint that their line shapes have the same Gaussian/Lorentzian line shape ratio and that the bridging/nonbridging oxygen ratio be 60/40. The positions and widths of the bridging oxygens, however, were treated as independent fit parameters in each spectrum. In all, this is a 23 parameter simultaneous fit of all five spectra. The result of this fit is displayed on Figure 2 and detailed in Table 3.

It can be seen from Figure 2 that the resulting fit is in good agreement with the experimental spectrum and that a binomial distribution (i.e. ideal solution) of cations around the nonbridging oxygens is a reasonable approximation. It must be stressed that this is not the only possible interpretation; however, it is one which is very consistent with a simple structural picture of cations distributed in random combinations around the non-

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### Table 3. Results of the fit Of The Isotropic Projection of the 2D \(^{17}\text{O}\) DAS Spectra of (a) \(v\)-K\textsubscript{100}Na\textsubscript{0}, (b) \(v\)-K\textsubscript{25}Na\textsubscript{75}, (c) \(v\)-K\textsubscript{50}Na\textsubscript{50}, (d) \(v\)-K\textsubscript{75}Na\textsubscript{25}, and (e) \(v\)-K\textsubscript{100}Na\textsubscript{0} Assuming A Binomial Distribution of Nonbridging Oxygen Sites

<table>
<thead>
<tr>
<th>Composition</th>
<th>(\delta) (ppm)</th>
<th>(\Delta\nu) (Hz)</th>
<th>(G\nu L)</th>
<th>Site Type</th>
<th>(\delta) (ppm)</th>
<th>(\Delta\nu) (Hz)</th>
<th>(G\nu L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(v)-K\textsubscript{100}Na\textsubscript{0}</td>
<td>16.1</td>
<td>1271</td>
<td>0.69</td>
<td>K\textsubscript{4}</td>
<td>68.7</td>
<td>896</td>
<td>0.94</td>
</tr>
<tr>
<td>(v)-K\textsubscript{50}Na\textsubscript{50}</td>
<td>16.0</td>
<td>1248</td>
<td>0.69</td>
<td>K\textsubscript{5}Na\textsubscript{1}</td>
<td>56.8</td>
<td>896</td>
<td>0.94</td>
</tr>
<tr>
<td>(v)-K\textsubscript{75}Na\textsubscript{25}</td>
<td>14.2</td>
<td>1396</td>
<td>0.69</td>
<td>K\textsubscript{4}Na\textsubscript{2}</td>
<td>45.4</td>
<td>896</td>
<td>0.94</td>
</tr>
<tr>
<td>(v)-K\textsubscript{25}Na\textsubscript{75}</td>
<td>13.9</td>
<td>1363</td>
<td>0.69</td>
<td>K\textsubscript{3}Na\textsubscript{1}</td>
<td>34.0</td>
<td>896</td>
<td>0.94</td>
</tr>
<tr>
<td>(v)-K\textsubscript{100}Na\textsubscript{0}</td>
<td>11.7</td>
<td>1276</td>
<td>0.69</td>
<td>Na\textsubscript{4}</td>
<td>27.1</td>
<td>896</td>
<td>0.94</td>
</tr>
</tbody>
</table>

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provide a unique view of the alkali cation ordering around nonbridging oxygens in silicate glasses. Results presented here show high resolution oxygen spectra that are consistent with a random mixing of two alkali types on four sites around each nonbridging oxygen. These results preclude significant clustering of similar cation types and are generally supportive of models of the mixed alkali effect that involve blocking of cation migration pathways by “foreign” cations.16,18

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