Rapid communication

Quantification of five- and six-coordinated aluminum ions in aluminosilicate and fluoride-containing glasses by high-field, high-resolution $^{27}$Al NMR

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Abstract

Aluminum cation sites with five ($^5$Al) or six ($^6$Al) anion neighbors are minor species in aluminosilicate glasses that are interesting in models of structure, diffusion, and viscous flow. Using $^{27}$Al NMR, we present the first direct evidence for $^5$Al in a calcium-aluminosilicate glass without excess aluminum over charge-balancing cations, and quantify small concentrations of both $^5$Al and $^6$Al in several fluoride-containing aluminosilicate glasses. NMR techniques that enhance resolution by decreasing the effects of second-order quadrupolar broadening, including triple-quantum magic-angle spinning (3QMAS), analysis of spinning sidebands, and data collection at very high external magnetic fields (14.1 and 18.8 T), are particularly effective in accurately observing such species. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

In alkali- and alkaline-earth aluminosilicate glasses prepared at ambient pressure, conventional models of short-range structure generally assume that, unless the molar concentration of Al is in excess of that of the ‘charge-balancing’ cations, all Al cations have only four oxygen neighbors ($^4$Al). For example, in sodium- or calcium-bearing aluminosilicate glasses with $X_{Al}$ as mole fraction, only $^4$Al is expected when $X_{Al}/X_{Na} \leq 1$ or when $X_{Al}/2X_{Ca} \leq 1$. This assumption is clearly a good first approximation, as little clear and direct experimental evidence has been reported to the contrary, except for a very recent $^{27}$Al NMR study [1] and an earlier report [2], both on Mg-aluminosilicates with $X_{Al}/2X_{Mg} \approx 1$. $^{27}$Al NMR also has revealed considerable concentrations of Al with higher than four coordination in calcium aluminate, binary alumina-silica, and highly peraluminous ($X_{Al}/X_{K} \gg 1$) K-aluminosilicate glasses (see [3] for review, also [4–6]). In these systems, some $^5$Al and/or $^6$Al may be required by charge-balance considerations, as insufficient concentrations of lower charge cations are present to neutralize the negative charge on bridging oxygens in $^4$Si–O–$^4$Al or $^4$Al–O–$^4$Al linkages. High-coordinate Al can also reach high concentrations in aluminosilicate glasses with high-field strength modifier cations such as La$^{3+}$ and Y$^{3+}$ [7,8], and in aluminoborates and aluminophosphates [2,9].
Here we present the first direct evidence for the presence of small concentrations of $^{5}\text{Al}$ in CaAl$_2$Si$_2$O$_8$ glass, the structure of which has been studied extensively by other methods. This finding is particularly interesting, because interpretation of the recently observed anomalous concentrations of non-bridging oxygen (NBO) in this material, and the implications for the liquid-state viscosity, were made with the conventional assumption of 100% $^{4}\text{Al}$ [10].

Small concentrations of $^{5}\text{Al}$ and/or $^{6}\text{Al}$ have also been reported in aluminosilicate glasses containing added fluoride, even when quite 'peralkaline' ($X_{\text{Al}}/X_{\text{Na}} < 1$) [11,12]. Here, these species are apparently stabilized by the presence of one or more F$^-$ ions in the Al coordination shell. However, it has not been clear what fraction of F$^-$ is bonded to such sites, or what fraction, if any, is bonded to $^{4}\text{Al}$ sites. Recent high-resolution $^{19}\text{F}$ NMR studies of a variety of silicate and aluminosilicate glasses with added fluoride provide an opportunity to revisit this problem [13]. Here we present $^{27}\text{Al}$ NMR on these materials, and address the issue of detecting and quantifying small amounts of high-coordinate Al using a number of approaches, including data collection at newly-accessible ‘very high’ magnetic fields strengths (14.1 and 18.8 T), analysis of spinning sidebands for satellite transitions [4,5,14], and triple-quantum magic-angle spinning (3QMAS) NMR [15–17]. All three approaches provide enhanced spectral resolution by reducing the effects of second-order quadrupolar broadening, which has in the past severely hampered the interpretation of $^{27}\text{Al}$ MAS spectra of glasses.

### 2. Experimental

Spectra were collected on Varian Unity 400S (9.4 T magnet, 104.3 MHz for $^{27}\text{Al}$), and Varian INOVA 600 (14.1 T, 156.5 MHz) and INOVA 800 (18.8 T, 208.6 MHz) spectrometers, using a Doty Scientific 5 mm ‘supersonic’ MAS probe with Si$_3$N$_4$ rotors at the lower field and Varian/Che- magnetics 3.2 mm MAS probes with ZrO$_2$ rotors at the two higher fields. One-pulse acquisition with short pulses (typically 15–30$^\circ$ or about 0.2 $\mu$s) was used, except for 3QMAS spectra, where a ‘shifted echo’ pulse sequence was used, followed by shear transformation during data processing [18]. In 3QMAS experiments, excitation ($\approx$4.3 $\mu$s) and reconversion ($\approx$1.8 $\mu$s) pulses were carefully optimized on the glass samples to obtain maximum intensity. Sample spinning rates of 14 kHz (at 9.4 T) and 18–23 kHz (higher fields) were used. Delays between pulses were chosen to maximize signal-to-noise, and were in some cases as short as 0.05 s. No differential relaxation among different NMR peaks was observed. All spectra are referenced to external 1 M aqueous Al(NO$_3$)$_3$.

Glass samples, identical to those described recently [13,18], were produced by standard melt-quench techniques, except that sealed Pt tubes were used to prevent fluoride loss during melting of the sodium-aluminosilicates. About 0.1 wt% of cobalt oxide was added to accelerate spin-lattice relaxation. Compositions are given in Table 1; sample labels are modified from those used previously for clarity.

### 3. Results

Single pulse $^{27}\text{Al}$ spectra collected at 9.4 T (Fig. 1) are unresolved and show the asymmetric ‘tail’ to lower frequency typical of quadrupolar nuclides with wide distributions of quadrupolar coupling constants ($C_Q$). As is typical at this field, this ‘tail’ from the predominant $^{4}\text{Al}$ sites covers and obscures regions of the spectrum where small peaks for $^{5}\text{Al}$ and $^{6}\text{Al}$ might be expected. However, in samples An and An + F, 3QMAS spectra reveal the presence of small extra peaks at the known position for $^{5}\text{Al}$ (Fig. 2), as observed previously in oxide glasses by this technique [7,17]. We have not attempted to exactly quantify intensities, but the concentration of $^{5}\text{Al}$ is at about the 1% level in the fluoride-free An glass. This result is thus consistent with our recent report of no observable $^{5}\text{Al}$ in this sample at a 2% detection limit, collected with less signal averaging and less well-optimized experimental conditions [18].

At 14.1 T, the effect of second-order quadrupolar broadening is sufficiently reduced so that shoulders or even partially resolved peaks for $^{5}\text{Al}$
and possibly $^{6}\text{Al}$ are clearly visible in samples $\text{Ab} + \text{Na} + \text{F}$ and $\text{An} + \text{F}$ (Fig. 1), similar to what was previously reported for two fluoride-bearing Na-aluminosilicate glasses at this field [11]. Unexpectedly, a peak for $^{5}\text{Al}$ is not resolved in sample $\text{Ab} + \text{F}$ at this field, even though its F content is five times higher than that of $\text{Ab} + \text{Na} + \text{F}$. This probably results in part from the narrower $^{6}\text{Al}$ peak in the latter. Also, the added Na presumably creates a significant fraction of NBO that shift the mean peak up in frequency by about 3 ppm, leading to less overlap with the $^{5}\text{Al}$ resonance. Spectra of the satellite transition (±1/2–±3/2) spinning sidebands, collected with extensive signal averaging (up to $10^5$ pulses), are well defined for the Ca-aluminosilicates $\text{An}$ and $\text{An} + \text{F}$, but are poorly resolved for the Na-bearing samples. In the former, the reduced quadrupolar broadening of this transition leads to clear resolution of $^{5}\text{Al}$ peaks (Fig. 3), as has also been previously reported for other oxide glasses [4,5,19]. Intensities of sideband peaks for $^{5}\text{Al}$ are too low to allow fitting of the overall manifold of all sidebands [5]. If the mean $C_Q$ for $^{5}\text{Al}$ and $^{6}\text{Al}$

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### Table 1: Compositions of glass samples and NMR data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nominal mole (%)</th>
<th>$^{4}\text{Al}$</th>
<th>$^{5}\text{Al}$</th>
<th>$^{6}\text{Al}$</th>
<th>Area (%)</th>
<th>Max. (ppm)</th>
<th>Area (%)</th>
<th>Max. (ppm)</th>
<th>Area (%)</th>
<th>Max. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ab} + \text{F}$</td>
<td>7.5 7.5</td>
<td>22.4 56.5</td>
<td>42.0 54.5</td>
<td>54.5 0.5</td>
<td>54.5</td>
<td>0.5</td>
<td>54.5</td>
<td>0.5</td>
<td>54.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{Ab} + \text{Na} + \text{F}$</td>
<td>9.3 7.4</td>
<td>22.3 59.9</td>
<td>42.0 54.5</td>
<td>54.5 0.5</td>
<td>54.5</td>
<td>0.5</td>
<td>54.5</td>
<td>0.5</td>
<td>54.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{An} + \text{F}$</td>
<td>7.1 7.1</td>
<td>15.1 56.0</td>
<td>42.0 54.5</td>
<td>54.5 0.5</td>
<td>54.5</td>
<td>0.5</td>
<td>54.5</td>
<td>0.5</td>
<td>54.5</td>
<td>0.5</td>
</tr>
<tr>
<td>$\text{An} + \text{Na} + \text{F}$</td>
<td>7.7 7.7</td>
<td>15.4 61.5</td>
<td>42.0 54.5</td>
<td>54.5 0.5</td>
<td>54.5</td>
<td>0.5</td>
<td>54.5</td>
<td>0.5</td>
<td>54.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

$C_Q$ values assume that the quadrupolar asymmetry parameter ($\eta$) = 0.6, error range includes variation due to values of $\eta$ from 0 to 1.

Fluoride concentrations were confirmed by $^{19}\text{F}$ NMR [13]. Peak maxima and relative areas are from spectra of the central (1/2–1/2) transition at 18.8 T except as noted. $\delta_{iso}$ values assume that the quadrupolar asymmetry parameter ($\eta$) = 0.6; error range includes variation due to values of $\eta$ from 0 to 1.

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Fig. 1. $^{27}\text{Al}$ MAS spectra of glass sample $\text{An} + \text{F}$ at the external magnetic fields shown. Here and in Figs. 3 and 4, vertical scales (not shown) represent the intensity in arbitrary units, normalized to the maximum peak height in each spectrum.
sites are similar (leading to similar total numbers of sidebands for each), then integration of individual satellite sidebands would provide an estimate of the concentration of $[{\text{Al}}]$ of about 1.5%. If, as is suggested from previous 3QMAS studies, the mean $C_Q$ of $[4]{\text{Al}}$ is about 5 MHz and that of $[5]{\text{Al}}$ is about 3 MHz [17], then the concentration of the latter should be scaled down by 3/5 to yield an estimate of about 1% $[5]{\text{Al}}$. Comparison of the center of gravity of the $[4]{\text{Al}}$ satellite sidebands (68 ppm) to that of the central peak (52 ppm) yields the best estimate of the mean isotropic chemical shift ($\delta_{\text{iso}}$) of 66 ppm [20]. This same correction was applied to the $[5]{\text{Al}}$ satellite peak to obtain a value of 36 ppm for $\delta_{\text{iso}}$.

At 18.8 T, further reduction of the quadrupolar broadening leads to nearly Gaussian shapes for the main $[4]{\text{Al}}$ peaks (Fig. 4). The result is even better resolution of the minor $[5]{\text{Al}}$ and $[6]{\text{Al}}$ peaks, which are now clearly visible at least as shoulders in all four glasses. As at 14.1 T, these are particularly visible in the An + F and Ab + Na + F glasses, where baseline correction and integration allows the peak areas and thus the site populations to be directly estimated (Table 1). In sample Ab + F, the partially-resolved $[5]{\text{Al}}$ peak seems anomalously small compared to other compositions, suggesting that it may be unusually broad (wide range of $\delta_{\text{iso}}$ or increased $C_Q$), or that more $F^{-}$ is bonded to $[4]{\text{Al}}$ in this sample (see Section 4).

![Fig. 2. $^{27}\text{Al}$ 3QMAS spectra at 9.4 T for samples An and An+ F. Intensities in arbitrary units are shown by contour lines, which are drawn at 5% intervals from 87% to 7% of maximum intensity with added lines at 2%, 3% and 4% to accentuate small features. Horizontal and vertical scales show relative frequency in ppm. Projections in the ‘MAS’ dimension give somewhat distorted versions of the one-dimensional MAS spectra ($[5]{\text{Al}}$ is unresolved); projections in the ‘isotropic’ dimension are free of second-order quadrupolar broadening ($[6]{\text{Al}}$ is clearly resolved).](image)

![Fig. 3. $^{27}\text{Al}$ MAS spectrum at 14.1 T for sample An, showing a spinning sideband for the $\pm 1/2 \rightarrow \pm 3/2$ satellite transition. The spectrum is the sum of four consecutive sidebands (shifted by multiples of the spinning frequency and added to increase signal-to-noise) located well away from the central peak, with the frequency axis adjusted to the center frequency of the sideband manifold. The upper spectrum shows the vertical scale multiplied by 4.](image)
A plot of the center of gravity of the central transition peak vs the inverse of the square of the external field allows the estimation of mean values of $C_Q$ and of the isotropic chemical shift $d_{iso}$ for single, non-overlapped peaks [21]. These criteria are met for the $[4]Al$ peak in sample An, where $[5]Al$ and $[6]Al$ peaks are too small to compromise the center of gravity estimate, and for sample Ab + Na + F, where all three peaks are well separated (Table 1). This analysis was not done for the $[5]Al$ or $[6]Al$ sites, whose peak maxima at 18.8 T are given instead. However, because 3QMAS data suggest that the $C_Q$ values for these sites are relatively small [17], the reported values are probably at most 2–6 ppm lower than the true mean $d_{iso}$.

4. Discussion

An obvious conclusion from this study is that concentrations of high-coordinate Al species as small as a fraction of 1% can be observed in aluminosilicate glasses if techniques that enhance resolution are applied, such as 3QMAS and spinning sideband analysis or even conventional MAS at ‘very high’ fields (e.g., 14.1–18.8 T). The latter approach is perhaps most likely to give quantitative results for species concentrations: at lower fields, distorted Al sites with large local electric field gradients and hence high $C_Q$ values are more likely to produce peaks that are broadened enough to be inaccurately observed or even missed entirely. With respect to measuring isotropic chemical shifts, which are field-independent and thus most useful for structural correlation and comparison with theoretical models, even results at 18.8 T may need correction for the effects of quadrupolar coupling, which can be estimated from data collected at multiple magnetic fields or from spinning sidebands for satellite transitions.

The data on $[5]Al$ and $[6]Al$ concentrations presented here have bearing on several recently discussed aspects of glass structure and properties.

4.1. Non-bridging oxygens and oxygen triclusters

We recently presented $^{17}O$ 3QMAS NMR data for CaAl$_2$Si$_2$O$_8$ (An) glass, which revealed that about 4% of the oxygens are ‘non-bridging’, when conventional models suggest that none should be present [10]. Following arguments recently made to explain viscosity anomalies in aluminosilicate liquids [22], together with the lack of clearly observed $[5]Al$ or $[6]Al$ sites in the glass, we assumed that the NBO were balanced by the formation of oxygen triclusters shared by three AlO$_4$ or SiO$_4$ tetrahedra. Our finding here of about 1% $[5]Al$ in this glass is not enough to substantially change this conclusion, but certainly makes our picture of minor, high-energy structural species that may be significant in viscous transport even richer: as suggested some time ago from findings of $[5]Si$ in alkali silicate glasses [3,23], five-coordinate states
for network cations could serve as transition complexes in microscopic diffusion and flow events. The existence of $^{[5]}\text{Al}$ in CaAl$_2$Si$_2$O$_8$ glass is perhaps not surprising given recent findings of even higher concentrations of this species in Mg-aluminosilicates [1]; the lower concentration in the Ca-bearing glass is expected because of the lower field strength of Ca$^{2+}$ relative to Mg$^{2+}$ [7].

4.2. Fluoride speciation

Our recent study of $^{19}$F NMR spectra of fluoride-bearing aluminosilicate glasses [13] showed that some of the F$^{-}$ are bonded to Ca, Na, and possibly even Si, instead of only to Al as has generally been assumed [11,12]. For example, in sample Ab + Na + F, relative peak areas suggest that about 55–70% of F$^{-}$ is bonded to Al; in sample An + F, that fraction is about 65–80%. With that correction, mass balance considerations and the $^{[5]}\text{Al}$ and $^{[6]}\text{Al}$ concentrations in Table 1 allow the fraction of F$^{-}$ bonded to $^{[4]}\text{Al}$ sites to be estimated. If the observed $^{[6]}\text{Al}$ sites are in fact AlF$_5$ groups and $^{[5]}\text{Al}$ sites are AlF$_3$ groups, then in either sample Ab + Na + F or An + F, the fraction of F$^{-}$ on $^{[4]}\text{Al}$ would be 0–20%. The coincidence of the estimates for the two samples suggests that AlF$_5$ and AlF$_3$ may account for most or all of the Al–F bonding, as proposed in the first $^{27}$Al NMR studies of such materials [11,12]. On the other hand, if, as suggested by ab initio calculations of chemical shifts, the $^{[5]}\text{Al}$ peak actually represents AlF$_3$O$_2$ or other mixed-anion groups [24], then 20–40% (or more) of the Al–F bonds would have to be $^{[4]}\text{Al}$ groups.

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References