

The Structural Role of Lanthanum and Yttrium in Aluminosilicate Glasses: A ^{27}Al and ^{17}O MAS NMR Study

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Aluminosilicate glasses containing rare-earth and rare-earth analogue cations such as Y^{3+} and La^{3+} are interesting for a variety of technological applications, as well as for elucidating general principles of glass formation and structure. We present high-resolution ^{17}O and ^{27}Al NMR data on a series of lanthanum and yttrium aluminosilicates, which show the significant increase in concentrations of AlO_5 and AlO_6 groups caused by the smaller radii and higher field strengths of the modifier cation in the latter. Triple-quantum magic-angle spinning (3QMAS) spectra for both nuclides show much better resolution than standard MAS and demonstrate that the latter can give misleading results for compositional effects on speciation. Oxygen sites that resemble those in crystalline Y_2O_3 and La_2O_3 were not detected, suggesting that such extreme clustering is not significant in the compositions studied. The role of highly coordinated Al, and the configurational complexity generated by the formation of such species, is discussed.

Introduction

Silicate and aluminosilicate glasses that contain rare-earth elements have major technological importance in lasers, optical amplifiers, lenses, and other optical components. Aluminosilicate glasses containing high concentrations of chemically similar, high-field-strength cations, in particular Y^{3+} , have also received considerable attention because of their unusual properties, including high glass transition temperatures (T_g), chemical stability, low electrical conductivity, and near independence of T_g on composition.^{1–3}

In optical materials, studies of glass structure have focused on the immediate coordination environment of the rare-earth cation; for example, in recent findings, X-ray absorption spectroscopy (XAS) and NMR have given coordination numbers and constrained the extent of cation clustering.^{4–6} The complement to this picture is the effect of the rare-earth cation on the silicate network, which will have major consequences for solubility, liquid–liquid phase separation, and the liquid viscosity–temperature curve, all of which control the ability to make a useful glass of a desired composition. Obvious questions begin at the short range: Are rare-earth cations randomly dispersed in the network, or are they preferentially associated with cations that provide particular local charge environments, and energetic stabilization, such as Al^{3+} ? On the larger scale, are there compositional heterogeneities that may prefigure phase separation? How does a rare-earth cation affect the network speciation, its connectivity, and resulting bulk properties?

With respect to glass-forming ability and the properties of the precursor liquids, the most significant characteristic of rare-earth cations is their high field strength, which is taken here for ease of comparison as the ratio of the formal charge (3+) divided by the square of the sum of the oxygen radius (1.4 Å)

and that of the rare-earth elements in 6-fold coordination⁷ and which ranges from 0.51 for Ce^{3+} to 0.59 for Lu^{3+} . The diamagnetic La^{3+} (field strength = 0.50) and the rare earth analogue Y^{3+} (0.57) cover most of the expected range of rare-earth behavior; however, they of course lack 4f electrons and the relatively more subtle ligand field effects on bonding and coordination. The decrease in radius with increasing atomic number for the rare-earth elements often also results in a shift in coordination number from 7 or 8 to 6, which is seen in crystalline silicates and which is probably expected in glasses as well.^{8,9} All of these cations have much higher field strengths than more common network modifier cations (e.g., 0.19 for Na^+ and 0.33 for Ca^{2+}), falling at the low end of “intermediate” cations.¹⁰ Yttrium aluminosilicate glasses, at least, are known to have properties similar to those of actual rare-earth aluminosilicates.¹¹

From a structural as well as technological perspective, aluminosilicate glasses containing only a rare-earth element or analogue as a third component are especially interesting, as they fall outside the traditional range of glass formers, in which low field-strength cations act to either modify the network or balance the charge of network AlO_4 groups. Recent studies of yttrium aluminosilicate glasses using ^{27}Al NMR showed, for example, that a significant fraction of the Al is 5- or 6-coordinated.² ^{29}Si NMR and vibrational spectra suggested an unusual degree of network disorder, again related to the high field strength of the Y^{3+} cation.^{2,12} The high content of highly coordinated Al also makes such glasses potential analogues for aluminosilicates at high pressure, which certainly undergo coordination changes but which may be difficult to recover with unaltered structure from high-pressure experiments.^{13,14}

In this paper, we further explore the structure of such glasses, choosing both yttrium and lanthanum as third components to elucidate the effect of cation field strength within the range of actual rare-earth cations and to avoid the complications that unpaired electronic spins pose for NMR. We apply triple-quantum magic-angle spinning (3QMAS) NMR to obtain ^{27}Al

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TABLE 1: Nominal Compositions (mol %) of the Investigated Samples

sample name	SiO ₂	Al ₂ O ₃	La ₂ O ₃	Y ₂ O ₃
LAS118	80	10	10	
LAS316	60	30	10	
LAS226	60	20	20	
LAS152560	60	15	25	
LAS252550	50	25	25	
YAS152560	60	15		25
YAS226	60	20		20
YAS251560	60	25		15
YAS316	60	30		10
YAS252550	50	25		25
	¹⁷ O Enriched			
YAS-17O	50	25		25
LAS-17O	50	25	25	

spectra that are free from the distortions of the second-order quadrupolar effect^{15–17} and to obtain ¹⁷O spectra which provide a complementary view of the structure around the oxide anion. We find indeed that there are major effects on network speciation that vary considerably from Y to La and that place new constraints on the extent and type of compositional clustering.

Experimental Section

Sample Preparation. Y and La aluminosilicate glasses (Table 1) were synthesized by mixing fine-grained Al₂O₃, SiO₂, and either Y₂O₃ or La₂O₃ (predried at 900 °C), grinding in a boron carbide mortar, melting in a platinum crucible for 0.5–1 h at a temperature of 1600 °C, and quenching the melt in water. A lack of component volatility indicates that final compositions should be very close to nominal. All samples were checked by optical spectroscopy; samples with high La and Y content (≥25 mol %) were characterized by X-ray diffraction. No crystals were detected by either technique.

The ¹⁷O-enriched glasses (LAS-17O and YAS-17O; Table 1) were synthesized in the same way, but ¹⁷O-enriched SiO₂ (about 40% ¹⁷O) was used along with 0.1 wt % MnO to shorten the ¹⁷O spin–lattice relaxation times. These samples were melted under argon to avoid ¹⁷O–¹⁶O exchange with air. The resulting ¹⁷O-enrichment level of the glasses is approximately 10–15%, with the yttrium-containing sample having a lower ¹⁷O content than that of the lanthanum-containing sample.

The samples cover much of the glass-forming regions of the Y and La aluminosilicate ternary systems at temperatures up to 1600 °C.^{2,3,11} We also attempted to make glasses from two lutetium aluminosilicate compositions but did not succeed, presumably because the even higher field strength of Lu³⁺ (when compared to Y³⁺) decreases the glass-forming region.¹¹

NMR Experiments. All NMR experiments were performed on a modified Varian VXR 400S spectrometer operating at 54.226 MHz for ¹⁷O and 104.217 MHz for ²⁷Al. MAS spectra were recorded using a 5-mm probe (Doty Scientific Inc.) spinning the sample at a frequency of 15 kHz. For a selective excitation of the central transition ($-1/2 \leftrightarrow 1/2$), a $\pi/10$ pulse (0.2 μ s) was used. Typically, between 5000 and 10 000 (²⁷Al) or 10 800 and 86 400 (¹⁷O) FIDs with a relaxation delay of 1 s were recorded. The ²⁷Al chemical shift was referenced to an external 1 M Al(NO₃)₃ solution; the ¹⁷O chemical shifts are reported with respect to tap water.

Two different pulse sequences were used to obtain a triple-quantum/single-quantum correlation spectrum under MAS conditions (3QMAS spectra).^{15–17} The ¹⁷O 3QMAS spectra were obtained using a two-pulse sequence as described by Vega and Pines.¹⁸ In this $\beta_1(\phi_1)-t_1-\beta_2(\phi_2)-t_2$ sequence, β_1 and β_2 were

set to 8.3 μ s (360°) for YAS-17O and to 5.4 μ s (180°) for LAS-17O, respectively. The spectral width in both dimensions was chosen to be 100 kHz; 72 and 48 t_1 increments for YAS-17O and LAS-17O, respectively, were required to avoid truncation effects. A spinning frequency of 14.5 kHz was used. To obtain a sufficient signal-to-noise ratio, 2880 transients were necessary.

²⁷Al 3QMAS spectra were obtained using the shifted-echo pulse sequence consisting of two hard (ideally nonselective) pulses β_1 and $\beta_2(\phi_2)$ and a soft, selective pulse $\beta_3(\phi_3)$ which is applied after n rotor cycles τ_r : $\beta_1(\phi_1)-t_1-\beta_2(\phi_2)-n\tau_r-\beta_3(\phi_3)-t_2$. The first two pulses were 360° pulses with a duration of 4.2–4.5 μ s; the third pulse typically had a duration of 18–20 μ s (180°). The delay between the second pulse and the soft pulse was chosen to be as long as 15 rotor cycles (at a spinning frequency of 15 kHz) to avoid incomplete refocusing of the magnetization and the introduction of rotational artifacts. Typically, 48–64 t_1 increments were necessary for a spectral width of 50 kHz. For a signal-to-noise ratio sufficient to observe even signals with relatively low intensity, 1152 transients per increment were used.

This sequence was also applied in ¹⁷O 3QMAS experiments; the results (in particular, the observed peak shapes) were almost identical to those obtained with the two-pulse sequence described above.

The processing of the time-domain data set has been extensively described in the literature and was done with the RMN software package (P. Grandinetti, The Ohio State University).^{19–21} The last stage of the processing involved a “shear transformation” to ensure that the projection in the ω_1 (triple-quantum) dimension is isotropic. The isotropic chemical shift δ_{iso} and the quadrupolar coupling product P_q of the observed resonances could then be determined from the observed resonance positions in the single- and triple-quantum dimensions δ_{MAS} and δ_{3QMAS} , respectively, using the relationships for nuclear spin $I = 5/2$:

$$\delta_{3QMAS} = -(^{17}/_{31})\delta_{iso} + (^{10}/_{31})\delta_{2Q}$$

and

$$\delta_{MAS} = \delta_{iso} + \delta_{2Q}$$

where

$$\delta_{2Q} = 6000P_q^2/\nu_0^2$$

Here, δ_{2Q} (in ppm) is the second-order quadrupolar shift, which contains the term $P_q = C_q(1 + \eta^2/3)^{1/2}$, where $C_q = e^2qQ/h$ is the quadrupolar coupling constant and η is the asymmetry parameter of the quadrupolar coupling tensor.^{21,22} ν_0 is the Larmor frequency. In the two-dimensional spectrum as plotted here, lines of constant P_q have slopes of $-3^{1/2}/17$. The uncertainty in the determination of P_q is ± 0.2 MHz; the isotropic chemical shifts are determined within ± 1.5 ppm. Because the spectral resolution did not allow the determination of η , we have taken it as 0 and assumed that $C_q = P_q$ in the rest of our discussion. Given typical values of $\eta < 0.4$ for ¹⁷O in silicates,²³ this assumption should introduce an error of less than 0.1 MHz.

Results

²⁷Al MAS Spectra. In Figure 1 the ²⁷Al MAS spectra of the YAS series as a function of the Al/Y content (series A) and the Si content (series B) are displayed. The central transition region shown here has a rather asymmetric peak shape typical of those in aluminosilicate glasses, which is mainly determined by the

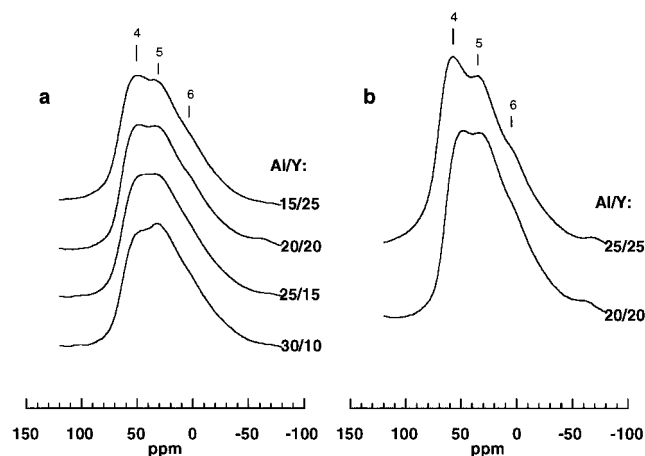


Figure 1. ^{27}Al MAS NMR spectra for yttrium aluminosilicate glasses. (a) Series A, with varying Al/Y ratios as shown. (b) Series B with varying SiO_2 content (50 and 60%) and fixed 1:1 Al/Y ratio. Peaks for 4-, 5-, and 6-coordinated Al are labeled. In these and other ^{27}Al spectra, spinning sidebands are well outside of the frequency range shown.

distribution of isotropic chemical shifts and of quadrupolar coupling constants. The spectra consist of at least two different peaks centered at about 50 and 35 ppm. The spectra of glasses YAS226 and YAS252550 show an additional shoulder at about 0 ppm. These three peaks are usually assigned to 4-, 5-, and 6-fold-coordinated aluminum (AlO_4 , AlO_5 , AlO_6).^{23–25} The latter species is not resolved in glasses of series A. In both series, an apparent change with composition of the relative intensity of the AlO_5 peak can be observed. In series A, this peak seems to increase in height with respect to the AlO_4 peak as the Al/Y ratio increases. In series B, the AlO_5 peak is apparently larger in the sample with the higher silica content. A similar trend is observed in the ^{27}Al MAS NMR spectra of the LAS glasses (not shown), but those spectra have significantly lower intensities in the region between 0 and 35 ppm than the respective spectra of the YAS series. At first glance, it is not clear whether the apparent change of the amount of 5- and 6-fold-coordinated aluminum as a function of Si content and Al/Y or Al/La ratio actually results from a change in species concentration or if it is due only to changes in the peak shape and the position of the predominant AlO_4 peak, or both. The spectra of the YAS glasses obtained here show some general similarities with spectra reported previously.² However, differences such as the relative intensities of 5- and 6-fold-coordinated aluminum were found which necessitated a more detailed investigation.

To better resolve the different species, it is necessary to remove the second-order quadrupolar broadening, which can be achieved by different methods such as double-rotation,²⁶ dynamic-angle spinning,^{27,28} or multiple-quantum spectroscopy, as used here. The latter two-dimensional spectra allow the separation of the second-order broadened pattern into a second dimension that is not affected by this contribution to the Hamiltonian and, hence, displays the isotropic lines broadened solely by distributions of chemical shift and quadrupolar coupling constants. All glasses were investigated using this method; two representative examples are shown in Figure 2. The spectrum of the yttrium-containing glass clearly shows three peaks attributable to AlO_4 , AlO_5 , and AlO_6 , but the lanthanum-containing glass shows only two peaks (AlO_4 and AlO_5), indicating that a possible peak of AlO_6 must have a low intensity (<5% of the total). This difference in the abundance of higher-coordinated aluminum, which was already noticed in the MAS spectra, is a general feature of our samples as illustrated in

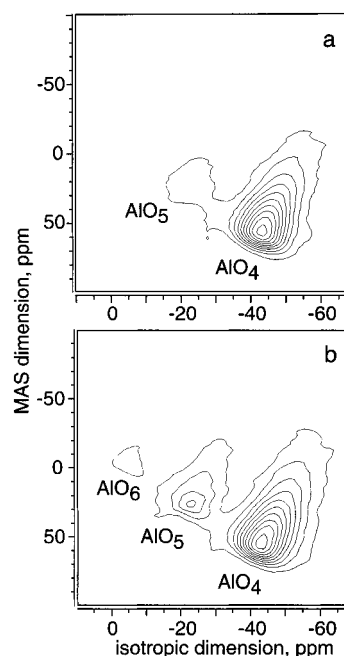


Figure 2. ^{27}Al 3QMAS for (a) LAS252550 and (b) YAS252550. The 10 contours display 5–95% of the total peak intensity.

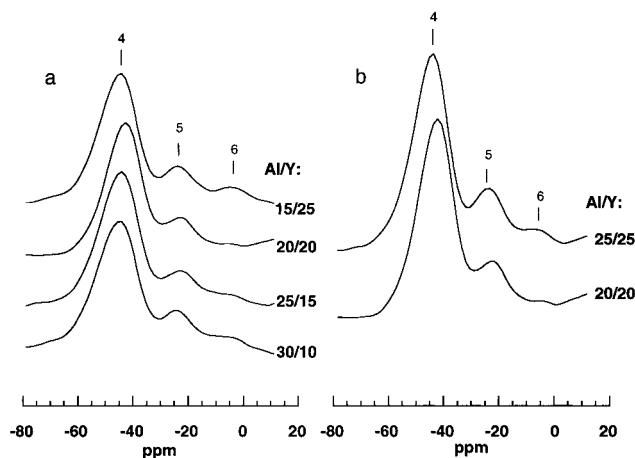


Figure 3. Isotropic dimension projections of ^{27}Al 3QMAS NMR spectra for yttrium aluminosilicate glasses. (a) Series A, with varying Al/Y ratios as shown. (b) Series B with varying SiO_2 content (50 and 60%) and fixed 1:1 Al/Y ratio. Peaks for 4-, 5-, and 6-coordinated Al are labeled.

Figures 3 and 4. In these figures, the projections along the isotropic dimension (i.e., the F1 dimension in the two-dimensional experiment) are displayed and provide several types of information about the abundance of the aluminum species as a function of composition. First, the spectra clearly confirm that YAS glasses contain more AlO_5 and AlO_6 units than the respective LAS glasses. In addition, the widths of the AlO_4 peaks for the LAS glasses are systematically less than those for the corresponding YAS glasses, suggesting a narrower range of δ_{iso} . Second, it appears that the relative concentration of each of the three aluminum species in the YAS glasses remains almost constant (within the error bars) when the Al/Y and the Al/Si ratios are changed. Small changes might exist in the abundance of AlO_6 species, but a detailed analysis of this peak is made difficult by its low intensity. Third, in the LAS glasses, the peak intensity for higher-coordinated aluminum increases slightly with (i) increasing Al/La ratio and (ii) increasing Al/Si ratio. Again, the 6-fold-coordinated aluminum is difficult to observe. These observations on the YAS glasses thus do not confirm previous

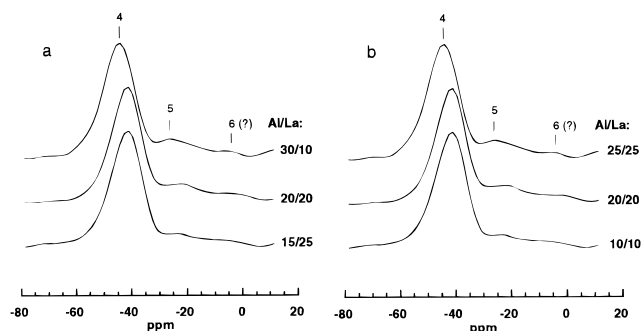


Figure 4. Isotropic dimension projections of ^{27}Al 3QMAS NMR spectra for lanthanum aluminosilicate glasses. (a) Series A, with varying Al/La ratios as shown. (b) Series B with varying SiO_2 content (50, 60, and 80%) and fixed 1:1 Al/La ratio. Peaks for 4-, 5-, and 6-coordinated Al are labeled.

results on glasses of similar composition;² the trends reported there rather agree better with the trends observed for our LAS glasses.

Isotropic chemical shifts and the quadrupolar coupling constants can be estimated from the two-dimensional spectra. The main difficulty with this approach is the asymmetry of the peaks, in particular those of the AlO_4 species. The values for δ_{iso} and C_q were determined using the peak maxima, keeping in mind that all peaks represent a distribution of δ_{iso} and C_q values. For AlO_4 , typical values for the central δ_{iso} are 64–69 ppm, with C_q from 5.0 to 6.0 MHz. The AlO_5 resonances have δ_{iso} of 31–35 ppm and C_q of 4.0–5.0 MHz. The values for AlO_6 have a larger error bar (because of the low intensity of the signals) and are estimated to be about 2 ppm and 3.0 MHz for δ_{iso} and C_q , respectively. The values are in agreement with other recent studies on aluminosilicate and aluminoborate glasses.^{21,29}

Figure 5 summarizes all δ_{iso} and C_q data for the AlO_4 and AlO_5 species in the YAS and LAS glasses. Within the relatively large uncertainties, compositional trends are generally subtle. It appears that the Al/Y ratio of the YAS glasses only slightly affects the ^{27}Al quadrupole coupling constant and the peak position in the MAS dimension. Only in the case of Al/Y = 3 does the AlO_4 species have a larger C_q and does the δ_{iso} of the AlO_5 resonance increase slightly. For the two glasses with Al/Y = 1, δ_{iso} of both resonances decreases with increasing SiO_2 content (i.e., lower aluminum and yttrium content) and C_q increases. In LAS glasses, both peaks also shift toward lower frequency with increasing SiO_2 content. With increasing Al/La ratio at constant SiO_2 content, δ_{iso} of the AlO_4 species shifts to lower frequencies, but δ_{iso} of the AlO_5 species shows the opposite trend. For C_q in the LAS glasses, the following trends were observed: (i) a slight increase for AlO_4 with increasing Al/La ratio and (ii) a decrease for AlO_5 with decreasing SiO_2 content at Al/La = 1.

^{17}O MAS Spectra. In Figure 6, the ^{17}O MAS spectra of two glasses are shown. Both are dominated by two roughly Gaussian shaped peaks. One major peak each was observed in the YAS glass at 54 ppm and in the LAS glass at 58 ppm. By comparison to recent ^{17}O NMR studies,^{28,30–33} this can be assigned to bridging oxygens (BO) joining two tetrahedral (T) cations. The 1:1 Si/Al ratios of these glasses suggest that Al–O–Si linkages should be the major contribution to this peak, although Si–O–Si groups must also be present because of the shift of considerable fractions of the Al into highly coordinated sites. Bridging oxygens connecting pairs of AlO_4 groups could also be present if the glass network structures are sufficiently disordered.

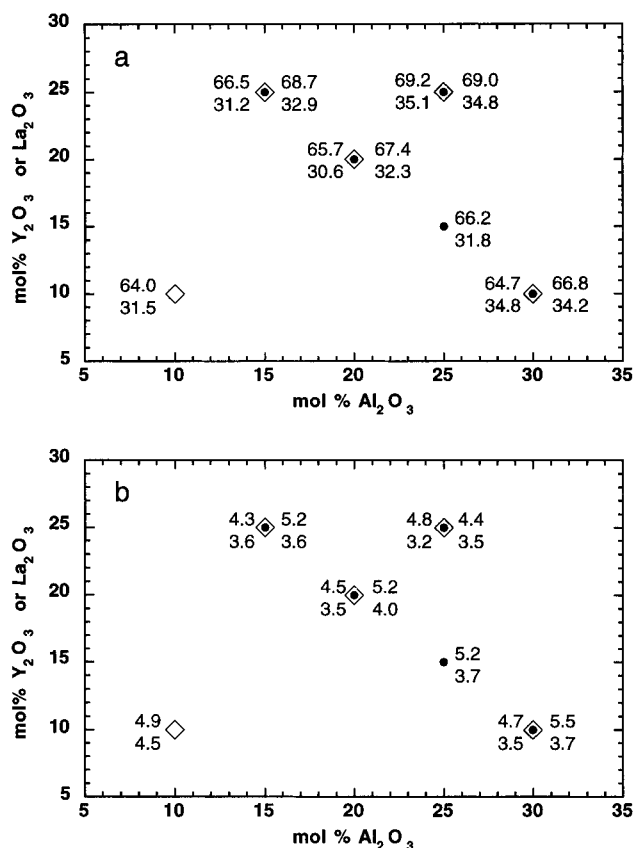


Figure 5. Compilation of (a) isotropic chemical shifts δ_{iso} and (b) quadrupole coupling constants C_q determined from 3QMAS spectra of LAS (open diamonds) and YAS (filled circles) glasses. The data represent the values for AlO_4 (top line), AlO_5 (bottom line), LAS (left of the symbols), and YAS (right of the symbols) glasses.

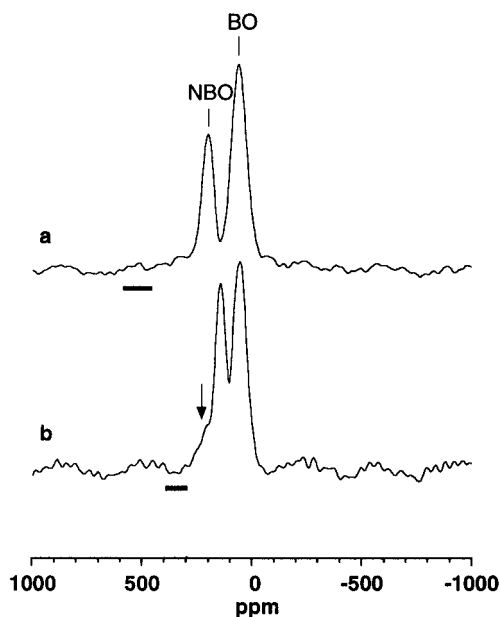


Figure 6. ^{17}O MAS NMR spectra for (a) LAS-17O and (b) YAS-17O glasses. Heavy lines show known ranges of peak positions for crystalline La_2O_3 and Y_2O_3 (see text). Bridging (BO) and nonbridging (NBO) oxygen peaks are labeled. The arrow shows the location of a third peak discussed in the text. Other low-intensity peaks are spinning sidebands.

The second, higher frequency peak is centered at 178 ppm for the LAS glass, and at 143 ppm for the YAS glass. This difference indicates that the oxygens contributing to this resonance must be at least in part coordinated by lanthanum or

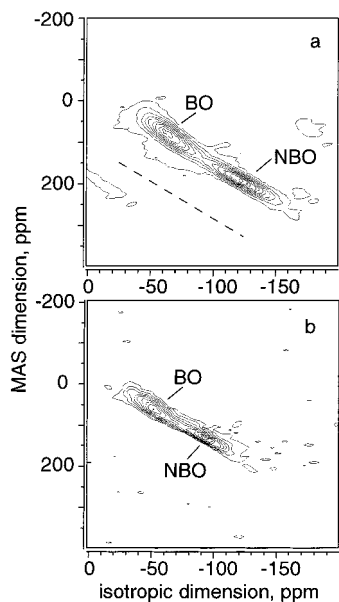


Figure 7. ^{17}O 3QMAS NMR spectra for (a) LAS-17O and (b) YAS-17O glasses. Bridging (BO) and nonbridging (NBO) oxygen peaks are labeled. The dashed line in part a shows a slope of $-31/17$, which is expected for a constant P_q with a distribution of δ_{iso} .

yttrium, respectively, and is most probably assignable to nonbridging oxygens connecting a single T cation with one or more Y or La cations. In the YAS glass, a third, partially resolved peak is present at about 210 ppm; this is tentatively assigned to nonbridging oxygens with more yttrium neighbors than those with a signal near 143 ppm (see Discussion). Repeated experiments and calculations of spinning sideband positions indicate that this feature is a real peak, not an artifact of the experimental conditions.

Neither spectrum shows a peak that can be assigned to oxygens in a La_2O_3 - or Y_2O_3 -like environment; i.e., there is no obvious signal from oxygen solely coordinated with yttrium or lanthanum at a detection limit above noise and sidebands of about 5%. Such peaks in the crystalline oxides have been shown to appear at 584–587 and 464–467 ppm for La_2O_3 ³⁴ (Florian, P. Personal communication) and between 313 and 383 ppm for Y_2O_3 .³⁵

The 3QMAS spectra of both glasses are displayed in Figure 7. In contrast to recently published ^{17}O 3QMAS spectra of Na and Ca aluminosilicate glasses,^{30,33} both peaks appear to be lined up along one diagonal with a slope close to $-31/17$, indicating a rather uniform quadrupolar coupling constant, with dispersion in the two dimensions dominated by wide ranges of δ_{iso} . The determination of C_q gave a value of 3.1 MHz for both samples. For the peak centers, δ_{iso} are 87-ppm (LAS) and 81-ppm (YAS) for the bridging oxygens and 200-ppm (LAS) and 150-ppm (YAS) for the nonbridging oxygens. The third component observed in the MAS spectrum of the YAS glass was not visible in the 3QMAS spectrum, however, probably because of a rather low signal-to-noise ratio because of the lower ^{17}O -enrichment level of this sample.

Discussion

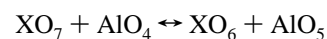
“Conventional” ternary aluminosilicate glasses (e.g., Na and Ca aluminosilicates) are generally considered to have a network of corner-shared AlO_4 and SiO_4 tetrahedra.¹⁰ Low-field-strength cations (e.g., Na^+ , Ca^{2+} , etc.) can play two roles. When their total charge is equivalent to the number of Al^{3+} cations (e.g., when $\text{Na}/\text{Al} = 1$ or $\text{Ca}/\text{Al} = 0.5$), then, ideally, all of oxygens

will be bridging oxygens and all of the low-field-strength cations will serve to compensate the net negative charge on BO connected to one or more AlO_4 groups (e.g., $-1/4$ net formal charge on an $\text{Si}-\text{O}-\text{Al}$ oxygen). Recent work has shown that this view is considerably oversimplified,³³ but it is still a useful starting point. As more of a “modifier” oxide (e.g., Na_2O or CaO) is added, nonbridging oxygens (NBO) form that are bonded to only one T cation and to several low-charge modifier cations.

As the field strength of the modifier cation increases, either through decreasing ionic radius or increased charge, it is expected to begin to perturb the aluminosilicate network more strongly, because of the energetic stabilization provided by closer association of negatively charged species, in particular NBO. Such cations may play an intermediate role between those of conventional network modifiers and network formers,¹⁰ but the exact nature of these effects is poorly understood, in part because of the relative difficulty of making glasses with high concentrations of such cations. La^{3+} and Y^{3+} provide interesting examples of such effects and are useful analogues for the effects of rare-earth elements in technological glasses. Although some NMR studies of ^{139}La and ^{89}Y have been made, it is difficult to obtain useful spectra for these nuclides in glasses for a variety of technical reasons.^{36,37} As reported here and in previous studies, it is thus most feasible to investigate the effects of such high-field-strength modifiers by observing the network species directly. ^{29}Si NMR spectra of YAS glasses are usually rather broad and featureless.² However, with increasing Y/Si ratio, the ^{29}Si peak shifts to a higher frequency, indicating a smaller shielding of the Si nucleus because of the substitution of Al by Y, which may be related to the conversion of BO to NBO. At the same time, peaks become narrower, suggesting an ordering of the network, resulting in a smaller chemical shift distribution. Earlier studies have already used ^{27}Al MAS NMR to demonstrate that one major effect of Y^{3+} is to promote the conversion of AlO_4 groups to higher-coordinate species.²

^{27}Al NMR. In all samples studied here, the most abundant Al species remains AlO_4 . Isotropic chemical shifts for this species, derived from 3QMAS, move to lower frequencies with increasing silica content (Figure 5), as expected from similar behavior for ^{29}Si shifts, and this is a result simply of increasing the average number of Si first-neighbor cations. This same effect is also present for AlO_5 and suggests that most of both species are mixed with SiO_4 in the structure; i.e., AlO_5 is not exclusively connected to Al or Y/La first-neighbor cations.

The most important effect of composition on the concentrations of the minority AlO_5 and AlO_6 species is their significant increase from La- to Y-containing glasses when pairs of the same stoichiometry are compared. This difference is expected from the considerably smaller size and higher field strength of Y when compared to La (0.57 vs 0.51 for 6-coordination, as defined in the Introduction). One way of illustrating this effect is as a “competition” for a small, tight coordination shell by oxygen between an “X” cation and Al^{3+} . X is shown as 6- or 7-coordinate for illustrative purposes only, and the resulting anionic charges are ignored. A similar reaction can be written for the formation of AlO_6 :



It is clear that reactions such as this are displaced to the right as the field strength of X increases. This effect is not limited to trivalent cations and is well-known in crystalline oxides. Crystalline alkali and some Ca aluminates contain AlO_4 groups; some Ca aluminates contain AlO_6 .²³ The Mg aluminate spinel

(MgAl_2O_4) contains only AlO_6 when ordered but can be partially disordered to contain some AlO_4 ; La and Y aluminates contain AlO_6 exclusively. For glasses and melts that do not contain large excesses of Al over modifier cations, AlO_5 and AlO_6 are of low (or zero) concentration in alkali and Ca aluminosilicate ternary compositions;^{21,24,38} higher-coordinated Al begins to appear in Mg aluminosilicate liquids and glasses and becomes quite important in Y aluminosilicates.^{38–40} In aluminous glasses with high concentrations of a second, unusually high field-strength network-forming cation such as B^{3+} or P^{5+} , high concentrations of AlO_5 and AlO_6 may also be present.^{21,41} P^{5+} can even “force” Si into 5- and 6-coordination in oxide glasses.⁴²

Quantification of absolute concentrations of aluminate species in ^{27}Al MAS NMR spectra is difficult because of the second-order quadrupolar broadening. This effect can make analysis of areas of multiple, severely overlapping peaks inaccurate even when intensities are in principle directly related to concentration. In some cases, analyses of spinning sidebands for satellite transitions (SATRAS⁴³) can be more effective, but this was not useful with the samples described here because of large chemical-shift distributions. Quantification of the two-dimensional 3QMAS spectra is also a complex problem. In this experiment, two coherence transfers take place: first, the transfer from a zero to the triple-quantum state and second, after the evolution period t_1 , the back-transfer into an observable single-quantum coherence. Both processes, in particular the latter one, depend on the quadrupolar coupling constant C_q and the applied radio frequency field. Sites with different C_q 's will show different efficiencies of the excitation of the triple-quantum states and, therefore, will have relative signal intensities which can differ significantly from the actual abundance of this site. If, however, the C_q 's of all observed resonances are similar, then a quantification is possible. For the relative effects discussed here, a much less stringent assumption is required: simply that any distortion of relative intensities caused by C_q differences is similar from one sample to another. The small variations with composition in C_q for each Al species (generally <10–20%; Figure 5) suggest that this should be valid. This conclusion is supported by recent ^{17}O 3QMAS NMR on oxide glasses, where similar variations in C_q lead to distortions of relative intensity of less than about 10–20%.⁴⁴

In the ^{27}Al MAS spectra of the YAS glasses, the relative intensity of the AlO_5 resonance seems to increase with increasing Al/Y ratio and increasing SiO_2 content. However, this trend is not supported by the respective 3QMAS spectra, in which the $\text{AlO}_4/\text{AlO}_5$ ratio, at least, appears to be roughly constant. For δ_{iso} and C_q determined from the 3QMAS spectra, this apparent discrepancy may be qualitatively explained in the following way: Increasing the SiO_2 content leads to a slight increase of the quadrupole coupling constants which results in a shift to lower frequency, which is particularly visible in the position of the peak maximum for the AlO_4 species. The change in intensity of the low-frequency side of the AlO_4 peak beneath the AlO_5 shoulder leads to an apparent increase in height of the latter. If the apparent discrepancy in compositional trends in $\text{AlO}_4/\text{AlO}_5$ ratios between MAS and 3QMAS spectra were caused by nonquantitative excitation of the AlO_4 peak in the latter, the opposite result would be expected. The same effect may be responsible for the intensity changes in glasses with 60% SiO_2 , in particular for the YAS316 glass. In addition to subtle and perhaps undetected changes in C_q , Figure 5 shows that the difference in δ_{iso} between AlO_4 and AlO_5 decreases significantly with increasing Al/Y. Again, the broad, asymmetric, low-frequency side of the AlO_4 MAS peak “pushes up”

the apparent height of the AlO_5 peak. MAS data alone may thus be quite misleading in assessing even qualitative changes in aluminate speciation, when MAS peaks are as broad and as overlapped as those described here. Ideally, a complete simulation of both MAS and 3QMAS spectra can lead to accurate quantitation,⁴⁵ but this approach may be difficult to apply to complex, disordered materials such as those discussed here.

In contrast, for the LAS glasses, both the MAS and 3QMAS spectra qualitatively show that the abundance of AlO_5 is dependent on composition: the relative intensity of the AlO_5 peak increases with decreasing SiO_2 content and with increasing Al/La ratio. It is likely, however, that the types of distortions in MAS spectra discussed above would affect any attempt at quantifying such changes.

^{17}O NMR. As in other silicate glasses that are relatively disordered, the bridging oxygen peak in the ^{17}O MAS spectra of the YAS and LAS glasses is nearly Gaussian in shape, lacking the well-defined quadrupolar doublet shape as seen in alkali silicates and in pure SiO_2 .^{46,47} It is considerably broader than that of glasses with lower field-strength charge-balancing cations, such as $\text{CaAl}_2\text{Si}_2\text{O}_8$ [about 80 vs about 45 ppm full width at half-maximum (fwhm)],³³ again presumably because of greater network disorder, possibly including Al–O–Al linkages. A similar difference is seen in the isotropic projections of ^{17}O 3QMAS data, where the fwhm of the BO peak in the YAS and LAS glasses is 30–40 ppm but only 19-ppm in $\text{CaAl}_2\text{Si}_2\text{O}_8$.

The C_q of BO in the YAS and LAS glasses (about 3.1 MHz) is significantly smaller than that determined by the same method for Si–O–Al in $\text{CaAl}_2\text{Si}_2\text{O}_8$ glass (3.5 MHz³³), which in turn is smaller than values in an Na-rich zeolite (3.7–4.1 MHz³²) and in $\text{NaAlSi}_3\text{O}_8$ glass (3.7 MHz⁴⁴). The cause of this systematic progression is likely to be the decreased strength of interaction with the BO from trivalent to divalent to monovalent cations, which in turn is expected to allow greater Si–O–Al bond angles and greater C_q values.^{27,48} Bond valence considerations suggest that a Si–O–Al oxygen should be bonded to no more than one Y^{3+} or La^{3+} cation.

The YAS and LAS glasses studied here by ^{17}O NMR are equimolar in Y_2O_3 or La_2O_3 and Al_2O_3 . If their structures were not complicated by the presence of AlO_5 and AlO_6 groups (on the basis of stoichiometry alone), they would have ratios of NBO/T cations of 1, because each Y^{3+} or La^{3+} cation can ideally charge-compensate three AlO_4 groups. This is contrary to what was apparently assumed in one recent discussion of similar materials.¹ The corresponding ideal ratio of NBO/total oxygen would be 0.4. It is clear that the second, higher frequency peaks in these spectra must therefore be dominated by NBO, that is, oxygens bonded to only a single T cation. The NBO peak for the YAS glass has a smaller δ_{iso} than that for the LAS glass, as expected from previously reported trends with varying cation size, such as Na^+ versus K^+ and Ca^{2+} versus Ba^{2+} .^{28,31} The NBO peaks may include oxygens bonded to AlO_4 or SiO_4 groups. Bond valency suggests that there should be two Y^{3+} or La^{3+} first-cation neighbors in either case.

More detailed analyses of the spectra, to address questions such as whether yttrium and lanthanum are preferentially attached to SiO_4 tetrahedra or to AlO_x ($x = 4–6$) polyhedra, are hindered by the relative lack of NMR data on appropriate model compounds. A first ^{17}O NMR study on crystalline phases in the $\text{La}_2\text{O}_3\text{--Al}_2\text{O}_3$ and $\text{Y}_2\text{O}_3\text{--Al}_2\text{O}_3$ systems (Florian, P. Personal communication), in which all Al is 6-coordinated, showed that with increasing number of Y^{3+} or La^{3+} cations attached to a 4-coordinated oxygen the ^{17}O NMR signal shifts

toward higher frequency. It is therefore reasonable to assume that the peak at 210 ppm in the YAS glass can be assigned to a nonbridging oxygen with three instead of two Y^{3+} neighbors. Simple bond-valence considerations indicate that an oxygen bonded to one SiO_4 group and to three Y^{3+} cations would be severely overbonded. Oxygens bonded to one AlO_4 group and three Y^{3+} could exist if the Y—O distances are unusually long, but an arrangement of one AlO_5 and three yttrium neighbors would be more favorable. In this case, such a site would not fit the usual definition of a nonbridging oxygen, as it would be bonded to no T cations. Confirmation of this assignment would be particularly interesting, as direct evidence for any such site in silicate glasses is very limited.⁴⁹

The lack of obvious ^{17}O NMR peaks for oxygen coordinated only by Y^{3+} or La^{3+} suggests that if there is an energetic tendency for these cations to separate from the network, it is not predominant. Energetic effects resulting from association of Y^{3+} with Al-containing groups may help to stabilize mixing, although direct evidence for this remains limited.

Structure—Property Relationships. As well as being analogues for rare-earth containing glasses, yttrium and lanthanum aluminosilicates are interesting because of their unusually high glass-transition temperatures (ca. 885–910 °C) and relative insensitivity of T_g to composition.¹ In a general sense, these properties may be understood as a result of the stronger bonding of the trivalent modifier cations when compared to conventional mono- and divalent cations and of the lower contrast in bond strengths between BO and NBO bonds when the latter involve a rare-earth element or analogue. However, aluminosilicate liquids containing only trivalent modifier cations are relatively poor glass formers, and their glass-forming range decreases with decreasing modifier cation radius,¹¹ potentially limiting their technological utility. Unfortunately, few complete sets of data on viscosity over wide temperature ranges are available on these liquids to help analyze their dynamics.

The presence of substantial fractions of three coordination states of Al is unusual in silicate glasses, and their mixing must make an unusually large contribution to the overall configurational entropy of the corresponding liquids. This effect will be larger for smaller trivalent modifier cations, which have higher concentrations of AlO_5 and AlO_6 groups. Increased overall disorder in the latter is also suggested by the greater ^{27}Al 3QMAS peak widths for the YAS versus the LAS glasses (Figures 3 and 4). These contributions to structural disorder may in part explain the increasingly poor glass-forming ability of higher field-strength modifier cations, as such an entropy increase may contribute to a more rapid decrease in viscosity above T_g .^{50,51}

Such an increase in network disorder with increasing modifier field strength appears to be a general phenomenon, whether it is measured in terms of silicate “ Q^n ” species having varying n of bridging oxygens, in terms of oxygen-species distributions,^{24,31,52} or in terms of aluminate speciation as described here. This trend correlates at least qualitatively with effects on both entropies of fusion and liquid heat capacities.⁵³ However, at the same time, higher field-strength modifier cations probably in some sense order their local oxygen coordination environments more effectively than lower field-strength cations.⁵⁴ Hence, the overall effect on configurational entropy will be complex.

A second important issue in the glass-forming ability of any multicomponent oxide liquid is the tendency to undergo liquid–liquid phase separation, as is known, for example, for the La_2O_3 – SiO_2 binary.⁵⁵ The increased configurational entropy

generated by the network disorder in the Y and La aluminosilicates should help to stabilize the liquid against phase separation, perhaps extending the useful compositional range.

Conclusions

The new technique of 3QMAS NMR provides higher resolution spectra for ^{17}O and ^{27}Al in glasses than conventional approaches and allows peak shapes to be more easily interpreted in terms of real distributions of structural parameters, unaffected by second-order quadrupolar broadening. A detailed comparison of Y and La aluminosilicate glasses shows that the higher cation field strength in the former tends to drive Al into higher coordination, yielding significantly higher fractions of both AlO_5 and AlO_6 groups and potentially having major effects on physical properties. Within each ternary system, effects on Al speciation of composition are apparently much smaller than those suggested by MAS spectra alone. ^{17}O data show no evidence for oxygen sites coordinated only by Y^{3+} or La^{3+} but do suggest that “oxide” sites coordinated only by Y^{3+} and 5- or 6-coordinated Al^{3+} may be present.

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