

Comparative ^{27}Al NMR and LAXS Studies on Rapidly Quenched Aluminosilicate Glasses

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Abstract

Aluminium site occupancies deduced from ^{27}Al NMR measurements of several aluminosilicate glasses of composition 35–60 mol% Al_2O_3 were used to calculate the mean coordination number, assuming two polyhedral models. In the models the 30 ppm Al NMR resonance was assigned to fivefold coordinated Al or to distorted tetrahedral units, respectively. Comparison of these mean coordination numbers with those derived from pair distribution functions (PDF) from X-ray scattering data of these glasses support the model in which the 30 ppm Al NMR peak is assigned to distorted tetrahedral units. This conclusion is also supported by simulations of the PDF line profiles using the NMR site occupancies and mean polyhedral bond lengths. © 1998 Elsevier Science Limited. All rights reserved

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1 Introduction

The structure of non-crystalline materials in the system $\text{SiO}_2\text{--Al}_2\text{O}_3$ has been a point of interest for many years. Unlike Si which is always tetrahedrally coordinated in these materials, coordination of Al is more complex. ^{27}Al NMR studies performed on non-crystalline aluminosilicates of various origins (i.e. glasses,¹ gels,² dehydroxylated kaolinite,³ PVD-coatings (our unpublished results), mechanically amorphised mullite⁴ and gibbsite (our unpublished results)) show signals at ≈ 0 ppm, corresponding to octahedrally coordinated Al ($\text{Al}^{[6]}$), at ≈ 60 ppm, corresponding to tetrahedrally coordinated Al ($\text{Al}^{[4]}$), and a third signal, often intense, centered at ≈ 30 ppm. Due to its intermediate position between $\text{Al}^{[6]}$ and $\text{Al}^{[4]}$ the 30 ppm

signal is often attributed to 5-fold coordinated Al;⁵ although it coincides with the isotropic chemical shift of 5-coordinated Al in well-characterized compounds, it does not show the characteristic quadrupolar peak shape and magnetic field dependence resulting from the presence of large electric field gradients (EFG's) associated with known $\text{Al}^{[5]}$ sites in crystalline compounds. Other possible explanations of this resonance have been advanced; Meinhold *et al.*³ and Peeters and Kentgens⁶ attributed the 30 ppm peak to $\text{Al}^{[4]}$ with elongated Al–O bonds rather than to $\text{Al}^{[5]}$, while Schmücker *et al.* have suggested that the origin of the 30 ppm peak are triclusters of (distorted) tetrahedra, i.e. three $(\text{Si,Al})\text{O}_4$ tetrahedra linked by one common oxygen atom.⁷ Such triclusters of tetrahedra exist in mullite ($3 \text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2$) and close structural similarities between mullite and its non-crystalline counterparts were deduced from similarities in the respective ^{27}Al NMR spectra and from the crystallization behaviour of the non-crystalline aluminosilicates.⁷

To shed further light on the nature of the Al species giving rise to the 30 ppm NMR resonance in non-crystalline aluminosilicates, rapidly quenched aluminosilicate glasses of various compositions were examined both by ^{27}Al NMR spectroscopy and by large angle X-ray scattering (LAXS), the results of which can be Fourier transformed to give the pair distribution function (PDF). The PDF contains information about all the interatomic distances, and when its analysis is restricted to the first maximum, it contains contributions from the next-nearest neighbour interactions only. However, the function profile is broad and diffuse, militating against its deconvolution into the various component interatomic distances. In this paper, an alternative approach was therefore adopted, in which ^{27}Al NMR spectroscopy was used to make a semi-quantitative determination of the fraction of the various Al–O polyhedra which were then combined with the appropriate interatomic distances and used

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to simulate a profile for comparison with the PDF lineshape. Two polyhedral models were considered: model 1 assumes the 30 ppm resonance is due to 5-fold coordinated Al, and contains Al^[4] (60 ppm), Al^[5] (30 ppm), and Al^[6] (0 ppm). Model 2 assumes that both the 60 and 30 ppm signals arise from AlO₄ tetrahedra of possibly different distortion, and contains only Al^[4] and Al^[6]. The average (Si,Al)-O coordination numbers calculated from the first PDF maximum were compared with those obtained from models 1 and 2, and this information, together with the comparison of the calculated and observed PDF profiles was used to deduce the likelihood that Al^[5] contributes to the first PDF maximum.

2 Experimental

2.1 Glass preparation

As the glass forming ability of aluminosilicate melts with Al₂O₃ contents > 10% is low, the melts must be ultra-rapidly quenched in order to suppress crystallization during the solidification process. Aluminosilicate glasses with 35, 50, and 60 mol% Al₂O₃ were obtained using a laboratory scale double-roller melt spinning apparatus as described elsewhere.¹

2.2 ²⁷Al MAS NMR

²⁷Al NMR spectra were obtained at 11.7 T using a Varian Unity 500 spectrometer and a 5 mm Doty probe spun at 10 kHz. Spectra were acquired at 130.3 MHz with a 15° pulse of 1 μs and a recycle time of 1 s and were referenced to Al(H₂O)₆³⁺.

2.3 PDF

X-ray scattering intensities were measured using a RINT 1200 diffractometer with Mo-K_α radiation. Data were collected by the $\Theta/2\Theta$ step scanning technique with 0.5° intervals in the range of 5 to 140° (2 Θ). Intensities were corrected for polarization, absorption, and Compton scattering using standard methods.⁸ Normalizations were carried out according Krogh-Moe⁹ and Norman.¹⁰ Atomic scattering factors were from International Tables of Crystallography¹¹ and Compton scattering factors were calculated using data of Hadju¹² and Palinkas.¹³ S-i(S) data, PDFs, and average (Al,Si)-O coordination numbers were calculated as described elsewhere.¹⁴ Densities of the glasses were measured by the heavy liquid technique.

3 Results and Discussion

²⁷Al spectra of aluminosilicate glasses with 60, 50, and 35 mol% Al₂O₃ are shown in Fig. 1. The

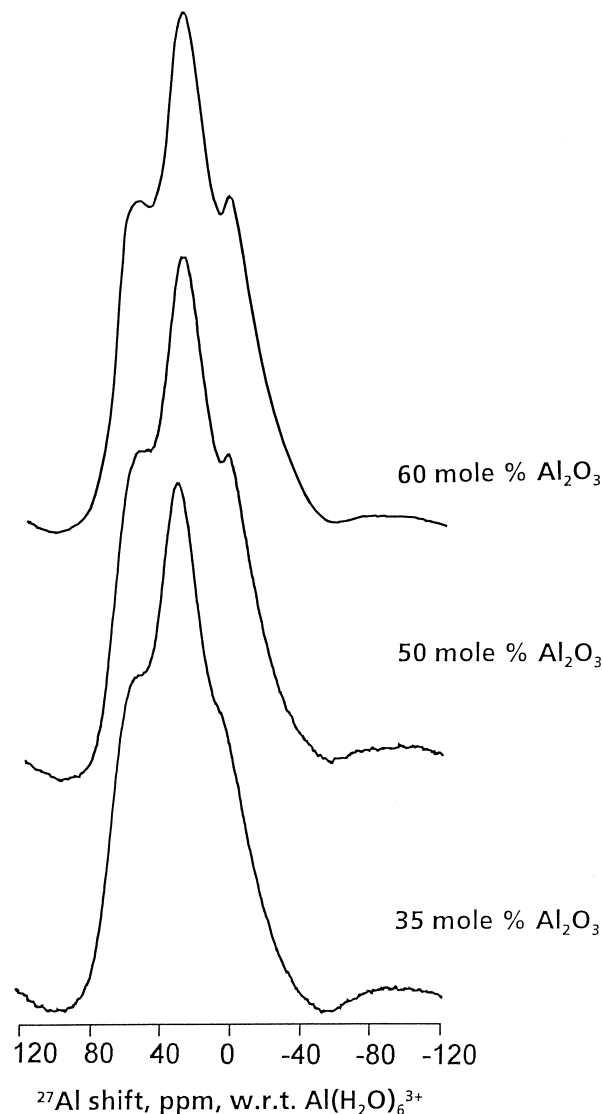


Fig. 1. 11.7 T ²⁷Al MAS NMR spectra of aluminosilicate glasses with 60 mol% Al₂O₃, 50 mol% Al₂O₃, and 35 mol% Al₂O₃.

spectrum of the most Al₂O₃-rich glass exhibits 3 well resolved peaks. Glasses with lower alumina contents show essentially the same spectra. However, peak resolution becomes poorer with decreasing Al₂O₃-content. Relative areas of the 0, 30, and 60 ppm spectral components were calculated by spectral deconvolution and confirming the 30 ppm Al-O species is the major component of these glasses. Mean values of deconvolution data obtained by several different fitting strategies show that about 20% of the observed aluminium occurs in the tetrahedral sites characterized by the 60 ppm signal, 55% of the Al corresponds to the 30 ppm signal, and about 25% of the Al is sixfold coordinated (0 ppm signal).

Figure 2 shows the PDF curves of aluminosilicate glasses with different Al₂O₃/SiO₂ ratios. The first PDF maximum which comprises all cation-oxygen distances shifts slightly towards higher interatomic distances with increasing Al₂O₃ contents.

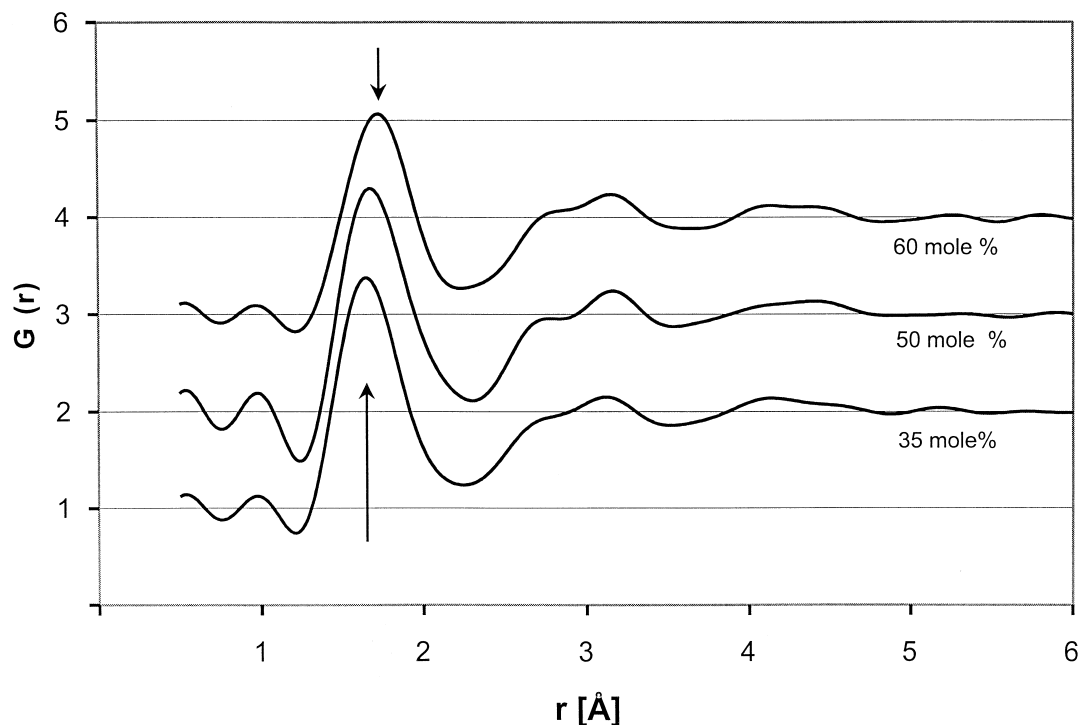


Fig. 2. Pair distribution functions (PDF's) derived from large angle X-ray scattering measurements of aluminosilicate glasses with 60 mol% Al₂O₃, 50 mol% Al₂O₃ and 35 mol% Al₂O₃. Arrows indicate the first maximum used in the present calculation.

Table 1 presents the mean coordination numbers of the different glasses according to model 1 (four-fold coordinated Si plus 20% of total Al in four-fold coordination, 55% of Al in fivefold coordination, and 25% of Al in sixfold coordination) and to model 2 (fourfold coordinated Si plus 75% of total Al in fourfold coordination and 25% of Al in sixfold coordination). These values are compared in Table 1 with coordination numbers obtained from the PDF data.

It is clear that the mean coordination numbers calculated on the basis of model 1, containing considerable amounts of Al^[5] are far greater than the values obtained from the X-ray data, whereas the mean coordination numbers calculated from model 2, containing only four- and sixfold coordinated Al, are much closer to the values resulting from the PDFs.

Figures 3–5 show the first PDF maxima of the aluminosilicate glasses fitted by either 4 gaussian functions according to model 1 (Si^[4]-O, Al^[4]-O, Al^[5]-O, Al^[6]-O) or by 3 gaussian functions according to model 2 (Si^[4]-O, Al^[4]-O, Al^[6]-O).

Table 1. Mean cation coordination number derived from models 1 and 2 compared with values derived from PDF data

Glass composition (mol% Al ₂ O ₃)	Model 1 (AlO ₄ , AlO ₅ , AlO ₆)	Model 2 (AlO ₄ , AlO ₆)	Calculated from PDF
60	4.80	4.38	4.3
50	4.70	4.33	4.2
35	4.54	3.26	4.1

Interatomic distances of Si^[4]-O (1.61 Å), Al^[4]-O (1.74 Å), Al^[5]-O (1.83 Å), Al^[6]-O (1.88 Å) were calculated from ionic radii.¹⁵ Since the atomic distances and the fractions of each site are fixed, the only fitting parameters were those associated with the broadness of the respective normal functions

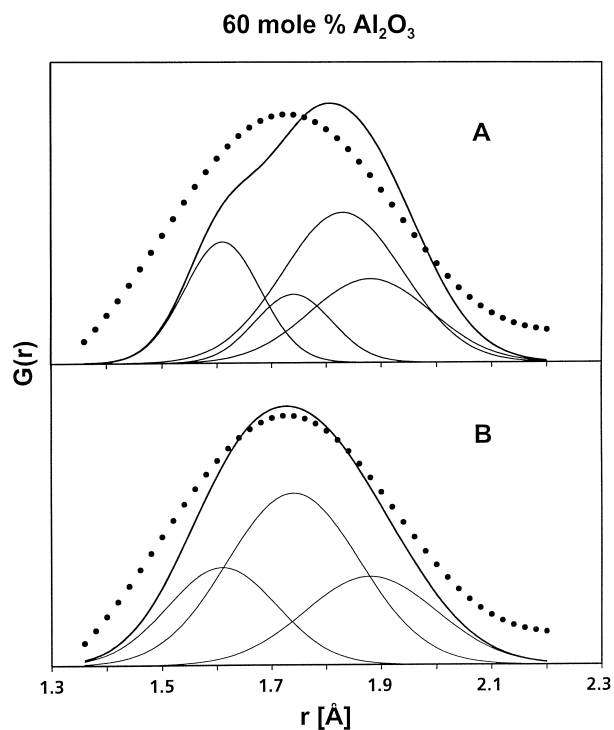


Fig. 3. Simulation of the first maximum PDF profile of 60 mol% Al₂O₃ glass (dots) by four gaussian functions according to model 1 (A) and by three gaussian functions according to model 2 (B).

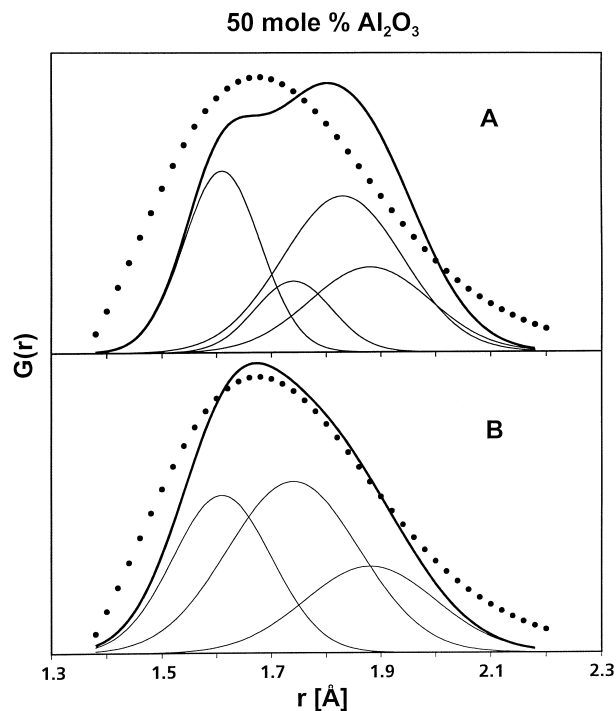


Fig. 4. Simulation of the first maximum PDF profile of 50 mol% Al_2O_3 glass (dots) by four gaussian functions according to model 1 (A) and by three gaussian functions according to model 2 (B).

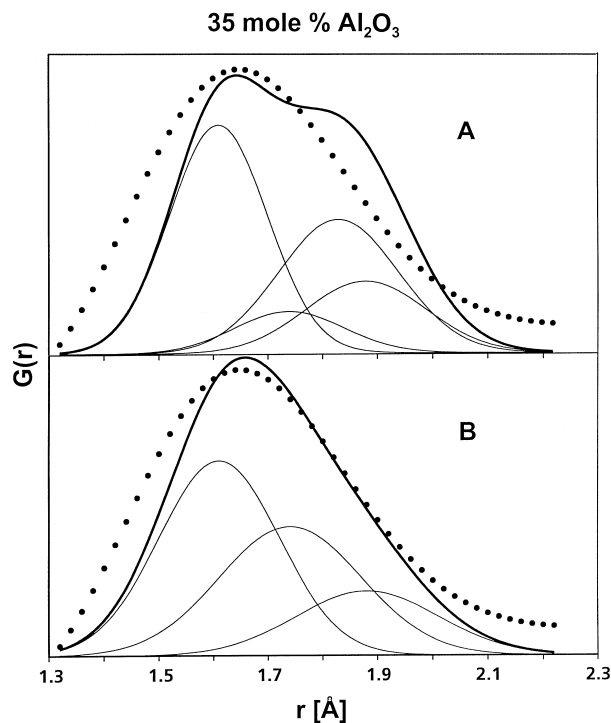


Fig. 5. Simulation of the first maximum PDF profile of 35 mol% Al_2O_3 glass (dots) by four gaussian functions according to model 1 (A) and by three gaussian functions according to model 2 (B).

(their standard deviation σ) and a global parameter fitting the sum of the individual normal functions to the PDF profile. The calculations clearly show that PDF data can be fitted well for all three glass compositions by taking into account only AlO_4 and AlO_6 polyhedra in addition to SiO_4 tetrahedra

(Figs 3B, 4B and 5B). On the other hand, if $\text{Al}^{[5]}$ is assumed to be related to the 30 ppm peak, and included in the fitting procedure, the shapes of the PDFs and the calculated distance distributions match poorly (Figs 3A, 4A and 5A). Moreover, the maxima of the calculated distance distributions occur at significantly higher values with respect to the PDFs.

4 Conclusion

The combined results of ^{27}Al NMR spectroscopy and PDF data for different glasses in the system Al_2O_3 - SiO_2 lead to the conclusion that a consistent interpretation can be made only if the 60 ppm peak of the ^{27}Al NMR spectrum and the 30 ppm peak are both attributed to fourfold coordinated Al. This suggests that two different kinds of AlO_4 tetrahedra might exist in non-crystalline aluminosilicates, of which the one giving rise to the 30 ppm signal possibly represents triclusters of distorted AlO_4 tetrahedra. The results are not consistent with the presence of AlO_5 in these glasses.

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