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R. Dupree, D. Holland, D. Williams. A MAGIC ANGLE SPINNING NMR STUDY OF THE EFFECT OF MODIFIER AND INTERMEDIATE OXIDES ON THE LOCAL STRUCTURE IN VITREOUS SILICATE NETWORKS. Journal de Physique Colloques, 1985, 46 (C8), pp.C8-119-C8-123. <10.1051/jphyscol:1985815>. <jpa-00225158>

HAL Id: jpa-00225158

<https://hal.science/jpa-00225158v1>

Submitted on 4 Feb 2008

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A MAGIC ANGLE SPINNING NMR STUDY OF THE EFFECT OF MODIFIER AND INTERMEDIATE OXIDES ON THE LOCAL STRUCTURE IN VITREOUS SILICATE NETWORKS

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Résumé: La sensibilité de la RMN (MAS) à la structure locale des matériaux amorphes a été mise à profit pour mettre en évidence la formation d'une distribution binaire Q^n/Q^{n-1} d'oxygènes non-pontants quand des oxydes modificateurs sont ajoutés à la silice. La position des raies de résonance de Si^{29} et Na^{23} varie avec la nature des autres modificateurs présents et est aussi sensible à la substitution par des oxydes intermédiaires responsables de l'existence d'associations de Na^+ avec $[AlO_4]^-$.

ABSTRACT: The sensitivity of MAS-NMR to local structure within amorphous materials is used to show the formation of a binary Q^n/Q^{n-1} distribution of non-bridging oxygens when modifier oxides are added to silica. The resonance positions of ^{29}Si and ^{23}Na are dependent upon the nature of other modifiers present and also on substitution by intermediate oxides, where evidence is presented for the association of Na^+ and $[AlO_4]^-$.

1. INTRODUCTION

Zachariasen /1/ proposed a set of criteria which might be used to describe a potential glass-forming system. These have been adapted over several years to become the, now widely accepted, random network model of glasses of the silica type. In this model, metal oxides are designated 'modifier' or 'intermediate' on the basis of their effect on the glass network as evidenced by changes in physical properties such as viscosity. These changes result from breakage of bridging oxygen [bo] links between silicon atoms in the network Si-O-Si to form non-bridging oxygen ions [nbo] Si-O⁻. Modifier oxides create [nbo] and intermediate oxides eliminate them on the basis of one [nbo] per unit valence.

Structural evidence for this can be obtained from vibrational spectroscopy /2/ and from techniques which probe the electron structure of the oxygen atoms such as O 1s XPS /3/. We have employed the technique of magic-angle-spinning NMR (MAS) to examine the effect of different oxide additions on the environment of ^{29}Si and ^{23}Na as indicated by their chemical shifts.

2. EXPERIMENTAL PROCEDURE

Samples were prepared by standard oxide glass melting techniques as reported earlier /4,5/. All glasses were rapidly cooled and not annealed.

The NMR spectra were mainly recorded on a Brüker WH400 spectrometer with the samples being rotated at the 'magic-angle' at a rate of 3 - 3.5 kHz. Details of accumulation procedure and data analysis have been discussed elsewhere for the two nuclei /4,5/.

3. RESULTS

3.1 Addition of modifier oxides

3.1.1. Silicon resonance

The [nbo] introduced by the modifier oxides could be distributed in the network in several ways which will give different concentrations of Q^n type silicon (Q^n represents silicon with n [nbo], n = 4 to 0 :-

- (a) a binary Q^n/Q^{n-1} distribution, where [nbo] are distributed evenly amongst silicon such that no more than two Q types exist in any composition;

- (b) a random distribution where the [nbo] are distributed statistically among the silicons and more than two Q types can co-exist;
- (c) clustering of [nbo] on individual silicons to give preferred Q^n species at given compositions.

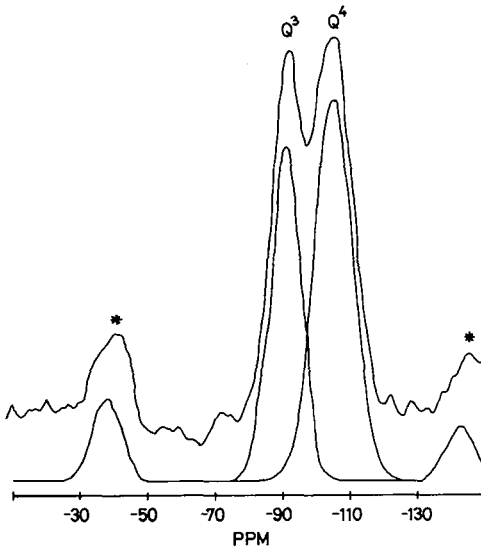
MAS-NMR can be used to identify Q^n , since the chemical shift of ^{29}Si is different for each value of n and can give quantitative information about Q^n compositions since the number of silicons of any Q type is given by the magnitude of the resonance. Second nearest neighbour effects can also be resolved.

Information for alkali-metal silicate glasses has been presented by several authors. For $\text{Li}_2\text{O}-\text{SiO}_2$, Schramm et al /6/ present evidence for a random [nbo] distribution whereas Grimmer et al /7/ interpret their data as supporting a binary distribution. It should be noted, however, that we regard the chemical shift data presented by both sets of workers as indicating that clustering and phase separation occur.

For $\text{Na}_2\text{O}-\text{SiO}_2$, both Dupree et al /4/ and Grimmer et al /7/ obtain data closely consistent with the binary distribution and a comparison between observed and simulated spectra for one sample is shown in Fig.1. At low concentration $\text{Rb}_2\text{O}-\text{SiO}_2$ and $\text{Cs}_2\text{O}-\text{SiO}_2$ also exhibit a binary distribution /5/ but at higher concentrations ≤ 45 mole %, Q^2 silicons become destabilised w.r.t. Q^3 and Q^1 and three peaks contribute to the total spectrum.

The chemical shifts of the individual Q^n species depend on the modifier oxide type. For the alkali metal oxides, the shift is found to be a function of the electronegativity of the metal /5/. In Fig.2 the changes in shift of Q^4 and Q^3 silicon resonances are plotted for 20 mole % $\text{Na}_2\text{O}-\text{SiO}_2$ glasses as part of the Na_2O content is replaced by CaO and similarly, for the shift of Q^3 in which CaO is added to a glass in which the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio is kept constant at 1:3. The abrupt discontinuity of the latter plot arises at the point where the Q composition changes from a Q^4/Q^3 to a Q^3/Q^2 binary distribution.

As well as affecting the chemical shift of silicon it is possible that changing the modifier cation might alter the distribution of [nbo] and hence the relative



quantities of the various Q species. At 20 mole % total modifier concentration, the Q^4/Q^3 ratio in $\text{Na}_2\text{O}-\text{Cs}_2\text{O}-\text{SiO}_2$ glasses is unchanged by substitution of Cs_2O for Na_2O . Veal et al /3/, using XPS measurements of [nbo] concentration, concluded that replacing Na_2O by CaO reduces the total [nbo] content and that only 80% of added CaO behaves as a typical modifier and the rest provide $-\text{Si}-\text{O}-\text{Ca}-\text{O}-\text{Si}$ cross links, i.e. intermediate behaviour. We have examined glasses of nominally the same composition as in the XPS study and analysed the Q^n/Q^{n-1} ratios which are sensitive indicators of [nbo] content. Best fits of the data were obtained for the two possible modifier contents and the closer agreement with calculated ratios was obtained for the case where all the modifier addition produced [nbo] which were then distributed on a binary basis. However, it should be noted that PbO in $\text{PbO}-\text{SiO}_2$ glasses does show a transition from modifier to intermediate behaviour, creating both [nbo] and $-\text{O}-\text{Pb}-\text{O}-\text{Si}$ links (to be submitted).

FIG.1. Observed ^{29}Si spectra from $20\text{Na}_2\text{O}.80\text{SiO}_2$ glass and (displaced below) the gaussian contributions from Q^4 and Q^3 silicons. Peaks marked * are spinning sidebands from Q^3 resonance.

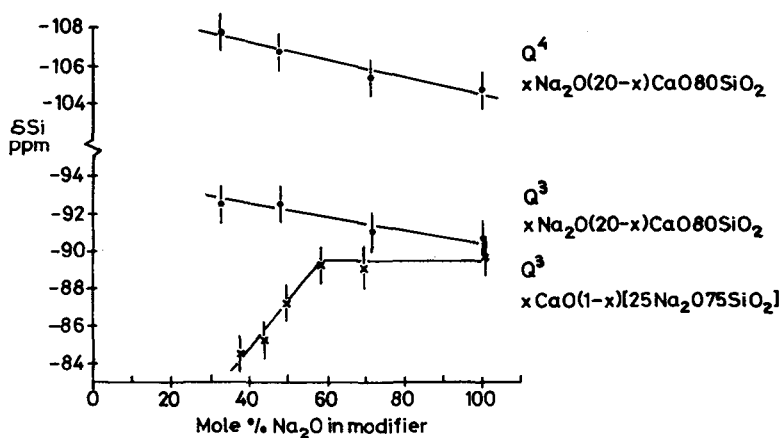


FIG.2 Effect of substitution of CaO for Na₂O on Q⁴ and Q³ positions in Na₂O-SiO₂ of various compositions.

3.1.2. Sodium resonance

The chemical shift of the ²³Na nucleus is complicated by the quadrupolar contribution, but changes in peak position can be observed when glass composition is altered. Fig.3 illustrates the change in ²³Na peak position in Na₂O-SiO₂ glasses with increasing Na₂O content and also on replacing Na₂O by Cs₂O or CaO.

In the binary glass there is a discontinuity in peak position at ~33 mole % Na₂O i.e. at the point where the silicon distribution changes from Q⁴/Q³ to Q³/Q², Fig.3a.

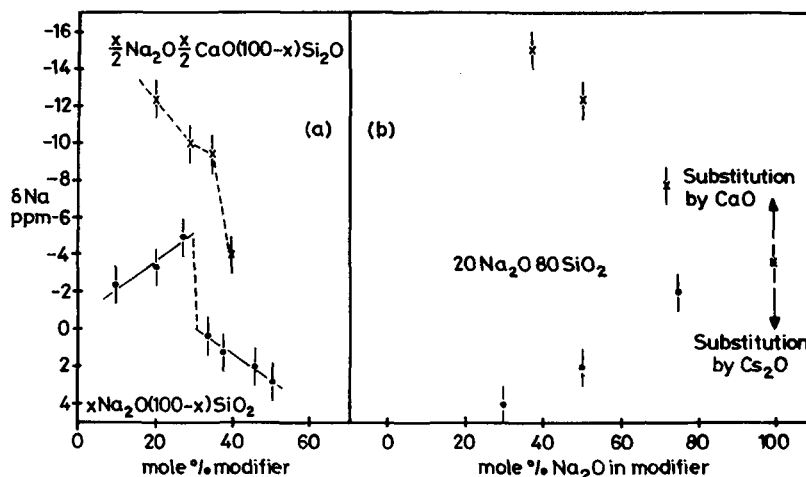


FIG.3. Effect of substitution of other modifier oxides for Na₂O on sodium resonance in Na₂O-SiO₂ glasses of various compositions.

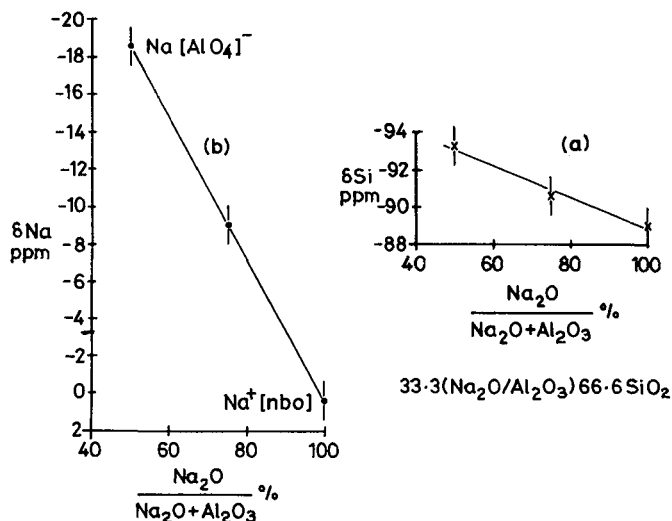


Fig.4 Effect of substitution of intermediate oxide Al_2O_3 for modifier oxide Na_2O on (a) silicon and (b) sodium resonances.

Replacing half the Na_2O by CaO almost eliminates this discontinuity and also changes the direction of slope below 30 mole % modifier. In Fig.3b, the effect of substitution of Cs_2O for Na_2O in 20 mole % modifier glasses is shown. The changes in peak position are nearly linear but in the opposite sense for the two cations, probably reflecting the different electronegativities ($\text{Na } 1.01, \text{Cs } 0.86, \text{Ca } 1.04$) or possibly different coordination preferences. Note, however, if the $\text{Na}_2\text{O}/\text{SiO}_2$ ratio is kept constant at 1:3 there is negligible effect of CaO substitution on the ^{23}Na resonance.

3.2 Addition of intermediate oxides

3.2.1 Silicon resonance

Al_2O_3 is the best known example of an intermediate oxide and this is assumed to enter the network and eliminate $[\text{nbo}]$ by the formation $[\text{AlO}_4]^-$ in which all the oxygens are bridging to other silicons or aluminium and the negative charge is delocalised. The second coordination sphere of silica may now contain either Si or Al, e.g. Q^3 , $[\text{Si}(\text{OSi})_3\text{O}]$ is replaced by a modified Q^3 $[\text{Si}(\text{OSi})_3(\text{OAl})\delta^-]$. The chemical shift of this modified species lies between those observed for normal Q^3 and Q^4 as illustrated in Fig.4a where the effect of replacing Na_2O by Al_2O_3 in 33.3 mole % $\text{Na}_2\text{O}-\text{SiO}_2$ (i.e. all Q^3) is to move the resonance to more negative shifts. At 50% substitution, i.e. 16.7 Na_2O , 16.7 Al_2O_3 , 66.6 SiO_2 the silicon environments should all be of the modified Q^3 type. The observed change in the chemical shift of silicon of ~4 ppm is comparable to that observed in zeolites when one silicon in the second coordination sphere is replaced by aluminium [8], providing confirmation of this particular Al distribution in the glass.

3.2.2 Sodium resonance

Replacement of $[\text{nbo}]$ by $[\text{AlO}_4]^-$ in the glass network means that sodium ions which would preferentially reside near the charged $[\text{nbo}]$ now are associated with the delocalised charge in the aluminate group. Fig.4b shows the considerable effect that this

change of environment has on the position of the sodium resonance -- lending support to the widely held view that $[\text{AlO}_4]^-/\text{Na}^+$ association occurs in these glasses.

4. CONCLUSION

MAS-NMR has shown that in binary alkali silicate and soda-lime-silica glasses a binary rather than a random distribution of Q type silicons is usual. Substitution of other modifier oxides for Na_2O changes the local environment of ^{29}Si and ^{23}Na in these glasses. This effect is not only determined by the amount of modifier added but also by the nature of the cation. When an intermediate oxide such as Al_2O_3 is added to the network, the ^{23}Na resonance gives strong evidence for association of Na^+ with the $[\text{AlO}_4]^-$ group in the glass.

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