Study of Borosilicate Glasses for Automobile Windscreens using Solid State NMR

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1 Background

- Automotive obscuration enamels used on rear windscreens must pass a new industry acid test.
- Enamels are made of the windscreen glass with a pigment added. They are used to protect the glue holding windscreens in place from degradation caused by UV light and hide electrical connections.
- Some of these materials are already commercially used, although their properties need to be improved.
- The group at Johnson Matthey are developing glasses with new compositions which have a high acid resistance and have a relatively low firing temperature of around 600˚C.

2 Aims

- The project will study the structure of these complex borosilicate glasses using multinuclear solid state nuclear magnetic resonance (NMR).
- NMR can be used to study the structural features on the atomic scale in order to learn how the local structure affects the properties of interest.
- Series of model glasses that maximise the desired structural characterisation will be made and studied.
- NMR will also be used to study materials produced using flame spray pyrolysis in order to understand the structural characteristics of these highly disordered materials.

3 Experiments

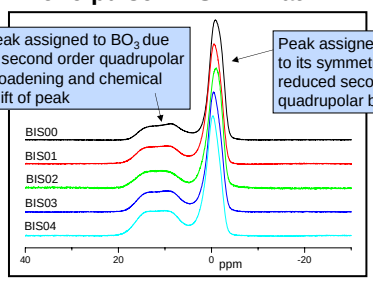
- Nuclei studied: spin ½ ^{29}Si; quadrupolar ^{7}Li, ^{11}B, ^{23}Na and ^{27}Al
- Multiple fields for ^{11}B (11.7 T and 7.05 T), ^{23}Na (14.1 T and 9.4 T) and ^{27}Al (14.1 T and 9.4 T); ^{29}Si studied at 7.05 T and ^{7}Li at 11.7 T
- MQMAS experiments carried out on ^{11}B; also possible for ^{27}Al

4 Samples

- Current research samples in commercial use – complex borosilicates.
- Model system of bismuth containing sodium borosilicate glasses.
- Devitrifying glasses containing crystalline phases formed during heat treatment.
- Glasses and other samples produced using flame spray pyrolysis.

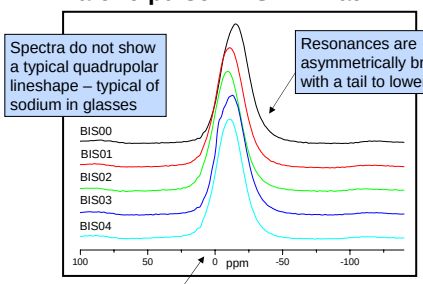
5 Results: Bismuth Model Samples

^{11}B one-pulse MAS NMR at 11.7 T



Spectra have been deconvoluted to obtain the relative intensities of the BO_3 and BO_4 peaks

^{23}Na one-pulse MAS NMR at 14.1 T



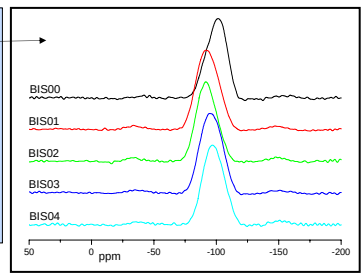
Position of the peaks:
- increases in frequency as the bismuth content is increased
- decreases in frequency as the boron content is increased

Sample compositions Mol%

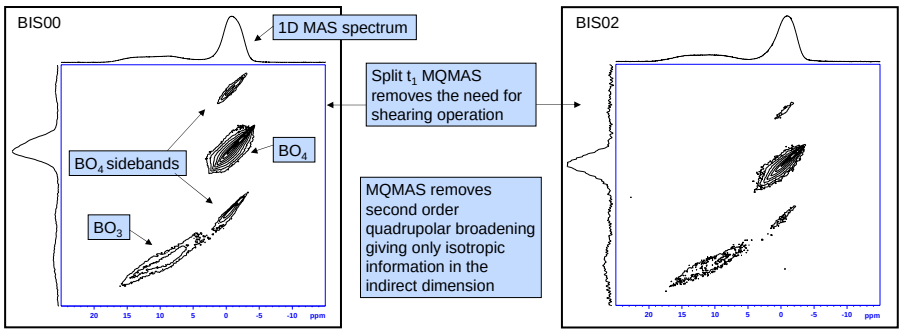
Sample	SiO_2	B_2O_3	Na_2O	Bi_2O_3	Al_2O_3
BIS00	55.5	30	14	0.1	0.4
BIS01	53	23	14	9.5	0.5
BIS02	55.5	13	13	18	0.5
BIS03	50	28	12.5	9	0.5
BIS04	47	24	11	17.5	0.5

^{29}Si one-pulse MAS NMR at 7.05 T

Spectra have been deconvoluted with 3 peaks which appear to correspond to Q_1, Q_2 and Q_3 units (the number is the number of bridging oxygen atoms



^{11}B MQMAS NMR at 11.7 T

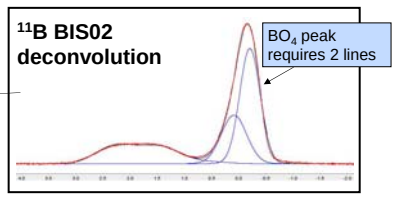


Split t_1 MQMAS removes the need for shearing operation

MQMAS removes second order quadrupolar broadening giving only isotropic information in the indirect dimension

This suggests that bismuth containing glasses have more than 1 BO_4 environment – investigated using MQMAS

^{11}B BIS02 deconvolution



6 Discussion

- Purpose of studying the bismuth model system: to discover whether bismuth and boron are related or independent in the glass network – does bismuth substitute boron?
- How does the network connectivity affect the acid resistance of the glasses?
- ^{11}B: The relative intensities of the BO_4 peaks increase as the amount of silicon in the sample increases. Silicon is a network former, it increases the network connectivity.
- MQMAS shows that both the BO_4 and BO_3 sites have chemical shift dispersion.
- ^{23}Na: The data suggest that when bismuth is substituted for boron the chemical shift of the sodium spectra increases. This implies that the network is less condensed. This suggests that bismuth is playing a network modifier role, whereas boron is a network former.
- ^{29}Si: The silicon deconvolutions show that there are several local environments.

7 Further Work

- On current samples: more data needs to be collected for comparison of multiple fields and MQMAS on ^{27}Al may be useful.
- A zinc model system can also be made similar to the bismuth system – sodium borosilicate glasses with varying amounts of zinc. This will determine whether zinc acts as a network former or a network modifier in these glasses.
- Similar data will need to be collected on further research samples from Johnson Matthey as their project develops.
- NMR on materials made by flame spray pyrolysis, including borosilicates similar to those produced by conventional methods for the rest of the project, bioglass, and ceramic materials such as aluminium oxide, zirconium oxide and cerium oxide.

THE UNIVERSITY OF WARWICK

JM Johnson Matthey

EPSRC Engineering and Physical Sciences Research Council