Solid State NMR Characterisation of Borosilicate Glasses
The Structure of Automobile Obscuration Enamel Glass

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1. Background

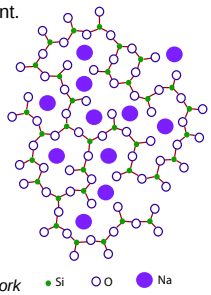
- Automotive obscuration enamels are used to protect the glue holding windscreens in place from degradation caused by UV light and to hide electrical connections. They are made of the windscreen glass with a pigment added.
- Enamels used on rear windscreens must pass a new industry acid test.
- Johnson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

2. Project

- The structures of these complex borosilicate glasses are studied 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.
- Samples: Current commercial and project samples; model samples and samples containing crystalline phases.
- Model glasses maximise the desired structural characterisation. Two sets of sodium borosilicates have been made, one containing bismuth and the other zinc, to investigate the role of these metals in the glass network.

3. Glass Networks

- Glass structure: an amorphous solid without long range periodic atomic arrangement.
- The structural units in the glass depend on the composition and affect the physical properties of the glass.
- Glasses are formed of oxides categorised as glass network formers or modifiers depending on their effect on the glass structure.
- In borosilicate glasses SiO_2 and B_2O_3 act as network formers – their cations form strong covalent bonds with oxygen.
- Alkali oxides such as Na_2O are network modifiers – the ions change the structure of the network as the cations only form bonds with the oxygen.[1]



Two dimensional representation of a sodium silicate network

4. Sample Compositions

Mol%

Zinc Model Samples

Sample	SiO_2	B_2O_3	Na_2O	ZnO
Z1	63.2	20.7	15.8	0
Z2	63.4	16.9	16.5	3.2
Z3	62.9	14.4	16.5	6.2
Z4	61.3	12.5	15.7	10.6
Z5	62.3	9.1	15.8	12.8
Z6	62.8	5.9	15.3	15.9
Z7	62.4	3.0	15.5	19.1
Z8	62.6	0	15.3	22.0

- Silicon and sodium ~ constant
- Boron plus bismuth / zinc ~ 21 %
- Bismuth / zinc increases as boron decreases

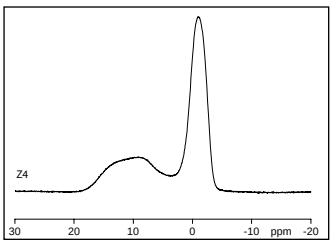
Bismuth Model Samples

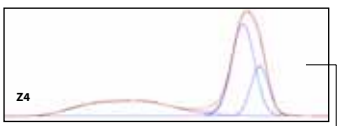
Sample	SiO_2	B_2O_3	Na_2O	Bi_2O_3
B1	63.2	20.7	15.8	0
B2	63.7	17.2	15.5	3.4
B3	63.7	14.3	15.1	6.4
B4	63.3	12.2	14.8	9.4
B5	63.5	8.8	14.8	12.5
B6	64.1	6.1	14.3	15.2
B7	63.8	3.2	14.4	18.2
B8	64.5	0.1	13.8	21.2
B9	61.7	0.1	13.6	24
B10	59.5	0.1	13.1	26.5
B11	56	0.1	12.4	29.8
B12	55.6	0.1	11.7	31.3

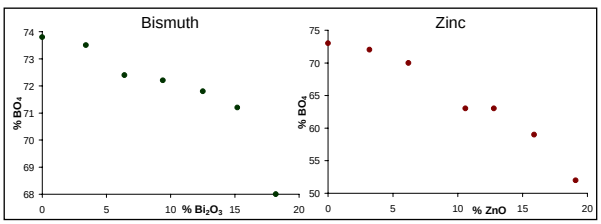
5. Model Samples: Experiments and Results

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

- All the spectra have 2 peaks
  - the peak on the left is assigned to BO_3 due to second order quadrupolar broadening and the chemical shift of the peak.
  - the right hand peak is assigned to BO_4 due to its symmetry which gives reduced second order quadrupolar broadening
- The terms BO_3 and BO_4 represent the two different environments in which boron is usually found.
- BO_3 is less stable than BO_4 due to an unoccupied 2p orbital[2] and forms less bonds in the network.
- The more BO_3 in a glass, the lower its temperature resistance.

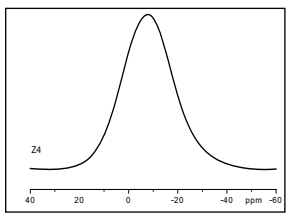




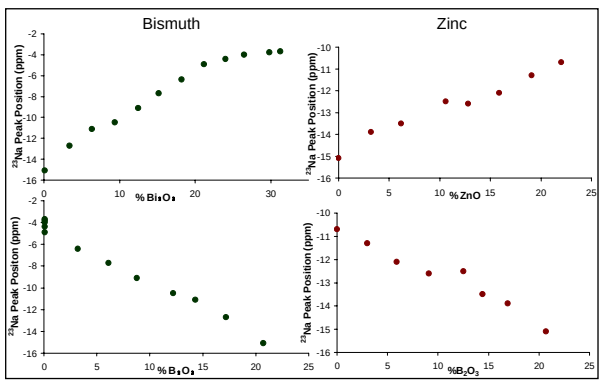


- ^{11}B Spectra have been deconvoluted to obtain the relative intensities of the BO_3 and BO_4 peaks.
- The BO_4 peaks need to be fitted with 2 Gaussian lines suggesting that these glasses contain more than one BO_4 environment.
- The relative amount of BO_4 decreases as the bismuth/ zinc content increases.

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

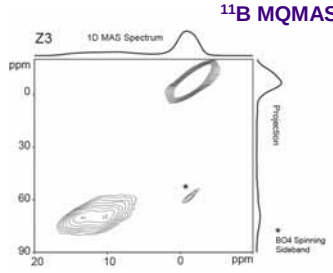


- The peak position of the sodium spectra changes with composition.
- The graphs of peak position against % B_2O_3 and % ZnO or % B_2O_3 show the same trends for both sample sets:
- The peak position increases with bismuth/ zinc content and decreases with boron content
- This implies the network becomes less condensed



6. Two Dimensional NMR

^{11}B MQMAS 14.1 T



- Preliminary 2 dimensional experiments have been done to investigate the BO_3 site further.
- One-pulse NMR allows deconvolution of the BO_4 peak.
- The BO_3 peak is harder to fit and may also contain more than one environment.
- Multiple Quantum Magic Angle Spinning experiments are used to obtain high resolution NMR spectra of quadrupolar nuclei.

7. Discussion

- Bismuth and zinc substitute boron in the compositions – do they also substitute it in the glass network by acting as network formers, or are they network modifiers?

Conclusions from the results:

- ^{11}B: the increase in the relative amounts of BO_4 with increasing bismuth / zinc shows that there are less bonds in the network. This implies that the glass network is becoming less connected and bismuth and zinc are not replacing boron as a network former.
- ^{23}Na: the increase in sodium peak position with increasing bismuth / zinc content implies that the Na-O distance is increasing causing the resonances to appear less shielded because the network becomes less condensed.[3] This suggests that both bismuth and zinc play a network modifier role.

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