Solid State NMR Characterisation of Borosilicate Glasses for Automobile Obscuration Enamels

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1. Background

- Enamels are used to protect glue holding windscreens in place from degradation by UV light and hide electrical connections.
- They are made from the windscreen glass mixed with a black pigment.
- They must pass a new industry acid resistance test.
- Johnson Matthey are developing glasses with new compositions which have a high acid resistance and the same firing temperature (around 600˚C) as conventional windscreen glass.
- Complex: higher acid resistance usually increases melting temperature.

2. Project

- Samples: Current commercial and Johnson Matthey project samples; model samples.
- Current research: Model glasses maximise the desired structural characterisation.

- Two sets of sodium borosilicate glasses, one containing bismuth and the other zinc, are being used to investigate the role of these metals in the glass network.

- Research question: Bi and Zn substitute boron in the compositions – do they also substitute it in the glass network by acting as network formers, or are they network modifiers?

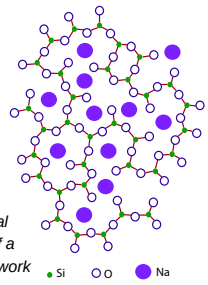
Model Samples

- Glasses contain SiO_2, B_2O_3 & Na_2O, and either Bi_2O_3 or ZnO.
- Silicon and sodium ~ constant.
- B + Bi or B + Zn ~ 21 %
- Bismuth / zinc increases as boron decreases.
- These samples were made by J. Higgs at the Johnson Matthey Technology Centre.

Magnetic Resonance Centre at Warwick University

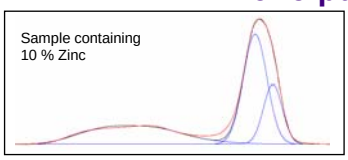
3. Glass Networks

- Glass structure: an amorphous solid without long range periodic atomic arrangement.
- Structural units in the glass depend on the composition and affect the physical properties.
- Formed of oxides categorised as network formers or modifiers depending on their effect on the 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 modifiers – the ions change the structure of the network as the cations only form ionic bonds with the oxygen.[1]



Two dimensional representation of a sodium silicate network

4. ^{11}B one-pulse MAS NMR

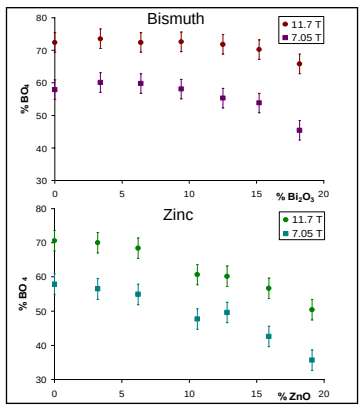


Deconvoluted ^{11}B spectrum

- Spectra have 2 peaks:
  - left peak: BO_3 - right peak: BO_4
- 2 environments in which boron is found.
- BO_3 is less stable than BO_4 - due to an unoccupied 2p orbital[2] it forms less bonds in the network.

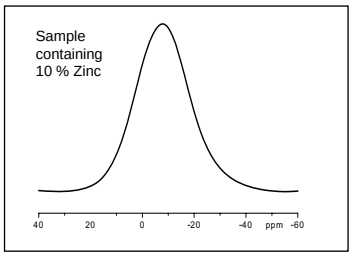
⇒ The more BO_4 in a glass, the higher its temperature resistance.

- Spectra are deconvoluted to obtain the relative intensities of the peaks.
- BO_4 peaks need to be fitted with 2 Gaussian lines ⇒ these glasses contain more than one BO_4 environment.
- BO_4 is plotted against Bi or Zn content.



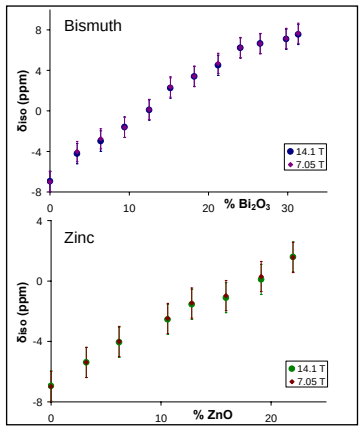
Decreasing BO_4 with increasing Bi or Zn shows that there are less bonds in the network ⇒ the glass network becomes less connected ⇒ bismuth and zinc are not replacing boron as a network former.

5. ^{23}Na one-pulse MAS NMR



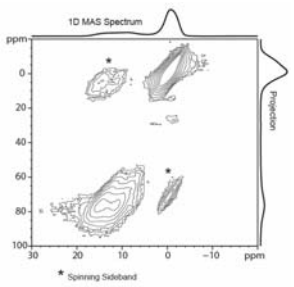
^{23}Na spectrum

- Graphs of peak position against % ZnO and % Bi_2O_3 show the same trends for both sample sets:
- Peak position increases with Bi or Zn content and decreases with boron content.



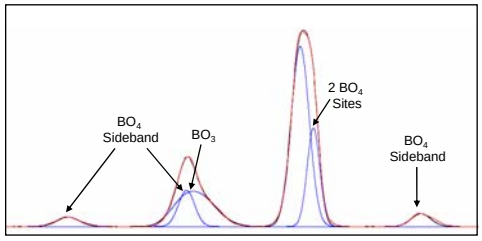
The increase in peak position with increasing Bi or Zn content implies that the Na-O distance is increasing, causing the resonances to appear less shielded because the network becomes less condensed.[3] This suggests that both bismuth and zinc play a network modifier role.

6. ^{11}B MQMAS & DOR at 14.1 T



MQMAS:
- Split t1 and z filter experiment.
- BO_4 peak shows a distribution of sites due to dipolar interaction.
- BO_3 also shows a distribution of sites.

DOR:
- Intended to improve deconvolution accuracy.
- Problem: BO_4 sideband overlays BO_3 peak.



7. Conclusions

- Analysis of the ^{11}B and ^{23}Na NMR data agree that neither bismuth or zinc are acting as network formers in these glasses

⇒ they both appear to act as network modifiers.

- The glasses contain a variety of structural units.

8. Further Work

- 1D ^{29}Si NMR has been carried out. ^{29}Si enriched samples will be made in order to investigate the silicon species in the glasses further with 2D ^{29}Si NMR.
- NMR parameters from MQMAS simulation will help refine structural models.
- Samples containing both Bi and Zn have been made in order to investigate the effects on the network of increasing one of these and decreasing the other.
- Other areas of the project in progress, samples made by Johnson Matthey.

References

1.A.K. Varshneya, Fundamentals of Inorganic Glasses, *Society of Glass Technology*, (2006).
2.D. Qiu, et al., *J. Mater. Chem.* (2008) 111 455-462.
3. X.Y. Xue, et al., *Phys. Chem. Miner.* (1993) 20 297-307.

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Johnson Matthey

Birmingham Science City ideasforlife

EPSRC Engineering and Physical Sciences Research Council

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