Solid State NMR Characterisation of Borosilicate Glasses for Automobile Obscuration Enamels

Johnson Matthey

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EPSRC Engineering and Physical Sciences Research Council

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

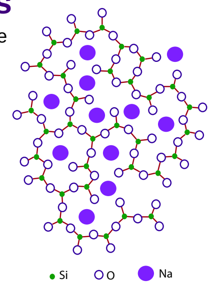
- Samples: Current commercial and project samples and model samples.
- Current research: Model glasses maximise the desired structural characterisation. Two sets of sodium borosilicates, one containing bismuth and the other zinc, are being used to investigate the role of these metals in the glass network.
- 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?

NMR Spectroscopy

- Local structures are studied using multinuclear solid state Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR).
- Correlates atomic scale features with the properties of interest.
- Requires a high magnetic field.
- Rapid sample rotation gives good resolution.

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 bonds with the oxygen.[1]



Two dimensional representation of a sodium silicate network

Samples

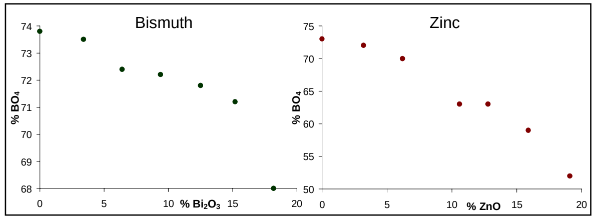
- Glasses contain SiO_2, B_2O_3, Na_2O and ZnO
- Silicon and sodium ~ constant
- Boron plus bismuth / zinc ~ 21 %
- Bismuth / zinc increases as boron decreases
- These samples were made by J. Higgs at the Johnson Matthey Technology Centre.

4. Results

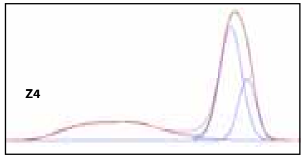
^{11}B one-pulse MAS NMR at 11.7 T

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

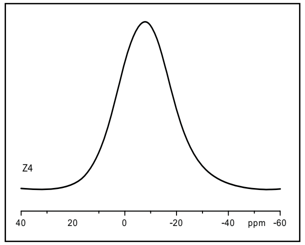
$\Rightarrow$ The more BO_4 in a glass, the higher its temperature resistance.
- Spectra are deconvoluted to obtain the relative intensities of the peaks.
- BO_4 peaks need to be fitted with 2 Gaussian lines - suggesting that these glasses contain more than one BO_4 environment.
- BO_4 is plotted against the Bi or Zn content.



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



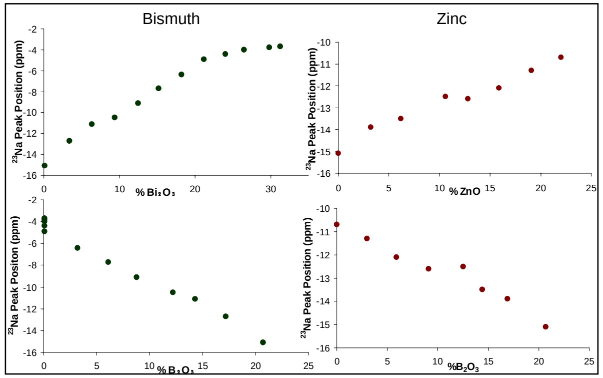
Deconvoluted ^{11}B spectrum



^{23}Na spectrum

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

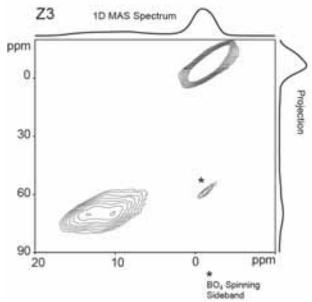
- Graphs of peak position against % B_2O_3 and % ZnO or % Bi_2O_3 show the same trends for both sample sets:
- Peak position increases with Bi or Zn content and decreases with boron content.



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.

Two Dimensional NMR

^{11}B MQMAS 14.1 T



- 2D experiments are being 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 MAS experiments are used to obtain high resolution NMR spectra of quadrupolar nuclei.

5. Conclusions

- The 1D NMR data show that both bismuth and zinc are not acting as network formers in these glasses – they both appear to act as network modifiers.
- 2D NMR is being used to examine the boron environments in more detail.

6. Further Work

- The compositions of these glasses are not commercially sensitive and so this work is publishable - multiple field NMR spectra have been collected and are currently being analysed for publication.
- Other areas of the project are also in progress such as JM samples containing fluorine, crystallising glasses, samples containing iron and samples made using flame spray pyrolysis.

References

1. A.K. Varshneya, Fundamentals of Inorganic Glasses, *Society of Glass Technology*, (2006).
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3. X.Y. Xue and J.F. Stebbins, *Phys. Chem. Miner.* (1993) 20 297-307.

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