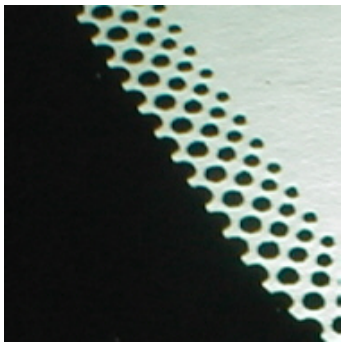
Solid State NMR Characterisation of Borosilicate Glasses for Automobile Obscuration Enamels

Jo Higgs



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  - Glass Structure
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JM Johnson Matthey

Background

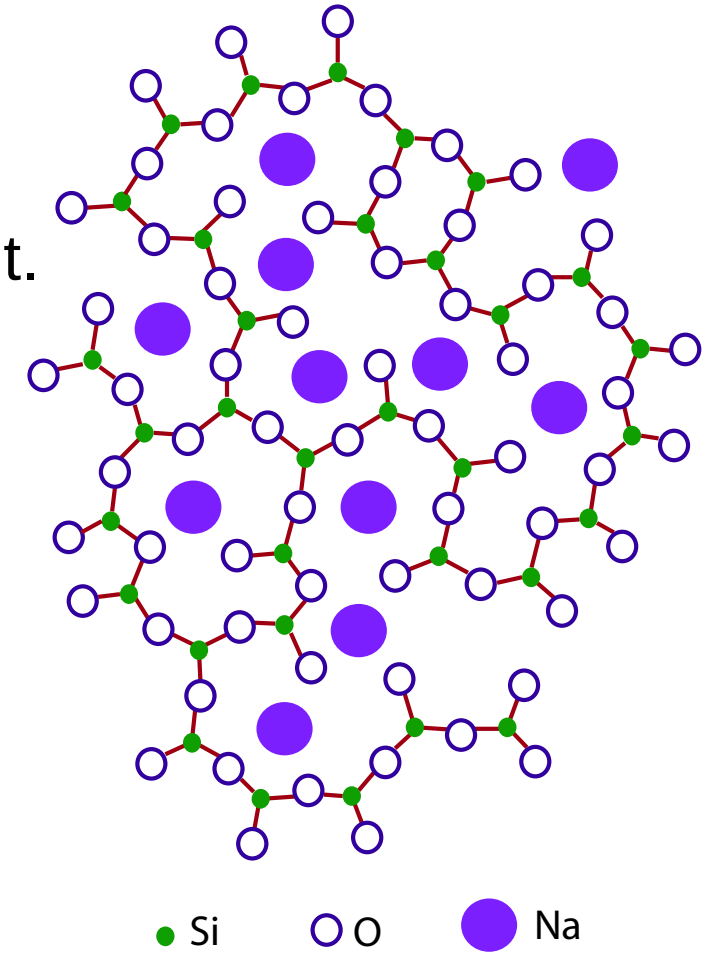
Johnson Matthey Windscreen Glasses

- Enamel
  - Windscreen glass with black pigment
  - Shield glue from UV light
  - Design
- New Product
  - Must pass new industry acid test
  - Increase acid resistance
  - Firing temp. ~ 600°C

Background

Glass Structure

- Amorphous solid without long range periodic atomic arrangement.
- Structural units
  - depend on the composition
  - affect the physical properties.
- Formed of oxides
  - network formers e.g. SiO_2 and B_2O_3
  - network modifiers e.g. Na_2O
  - intermediates



Zinc & Bismuth Model Samples

- Aim: Study the effects of Zn and Bi on the structure of sodium borosilicate glass

- Composition:
- Contain SiO_2, B_2O_3, Na_2O and ZnO or Bi_2O_3
- Si + Na ~ constant for all samples
- B + Zn or Bi ~ 21 mol%
- Zn / Bi increases as B decreases

Experiments:
- Single pulse: ^{11}B, ^{23}Na, ^{29}Si
- ^{11}B MQMAS
- ^{11}B DOR (one sample)

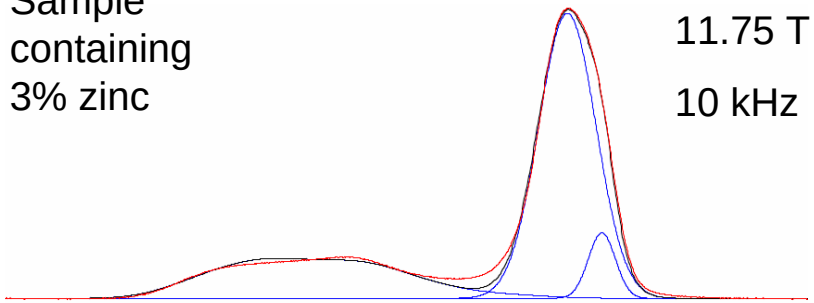
- Research question: Bi and Zn substitute B in the compositions – do they also substitute it in the glass network?

Model Samples – ^{11}B

Sample containing 3% zinc

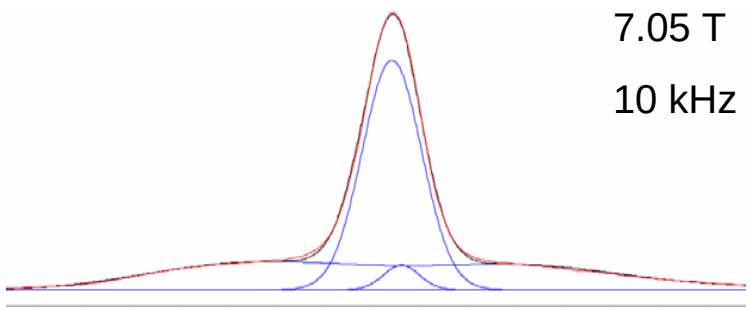
11.75 T

10 kHz

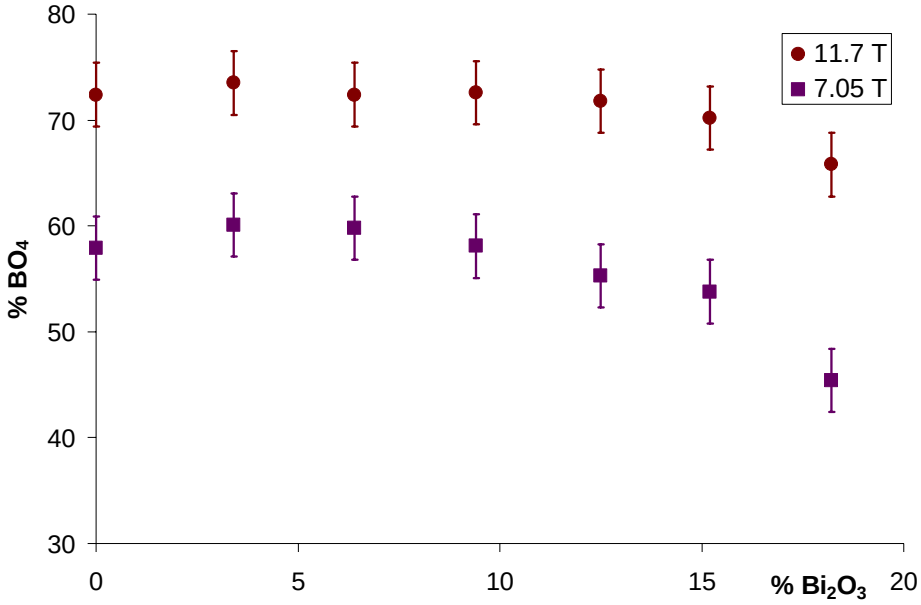


7.05 T

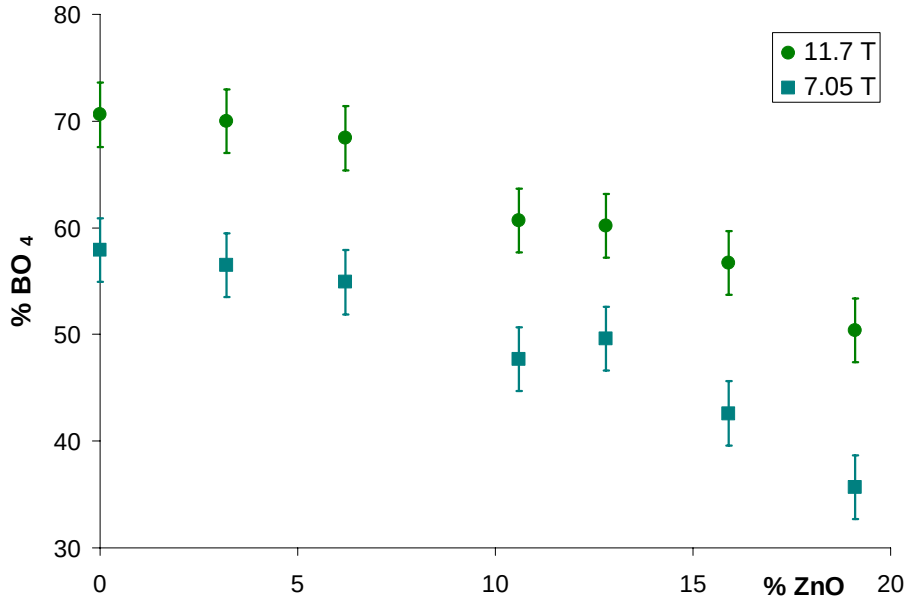
10 kHz



Bismuth Samples



Zinc Samples

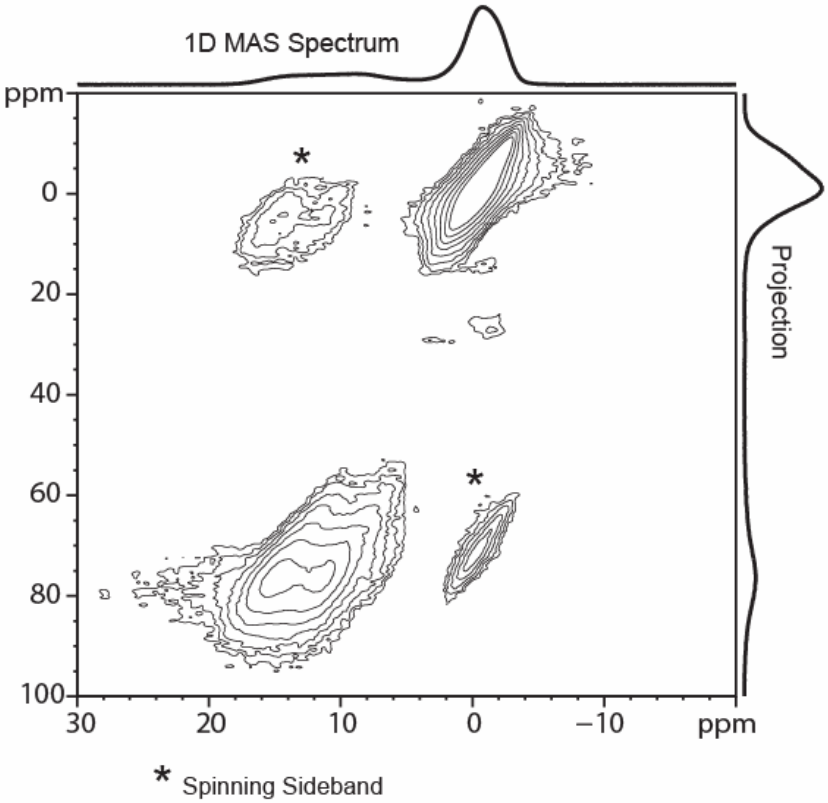


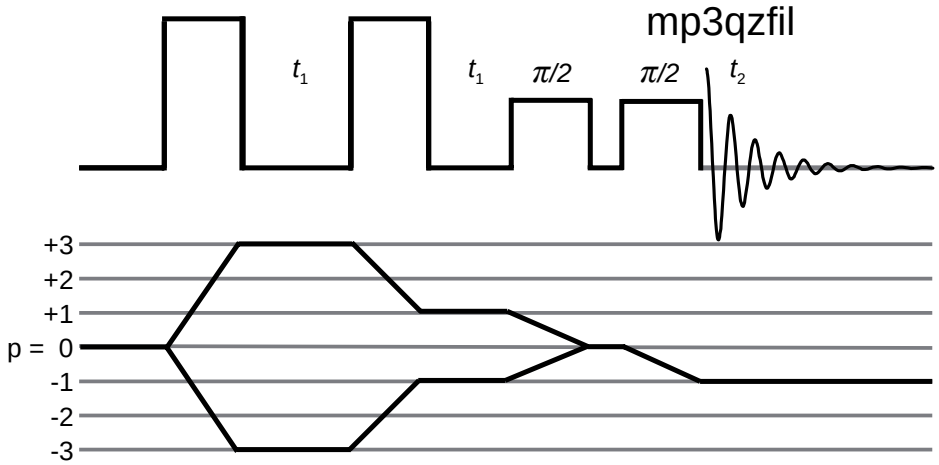
^{11}B – MQMAS & DOR

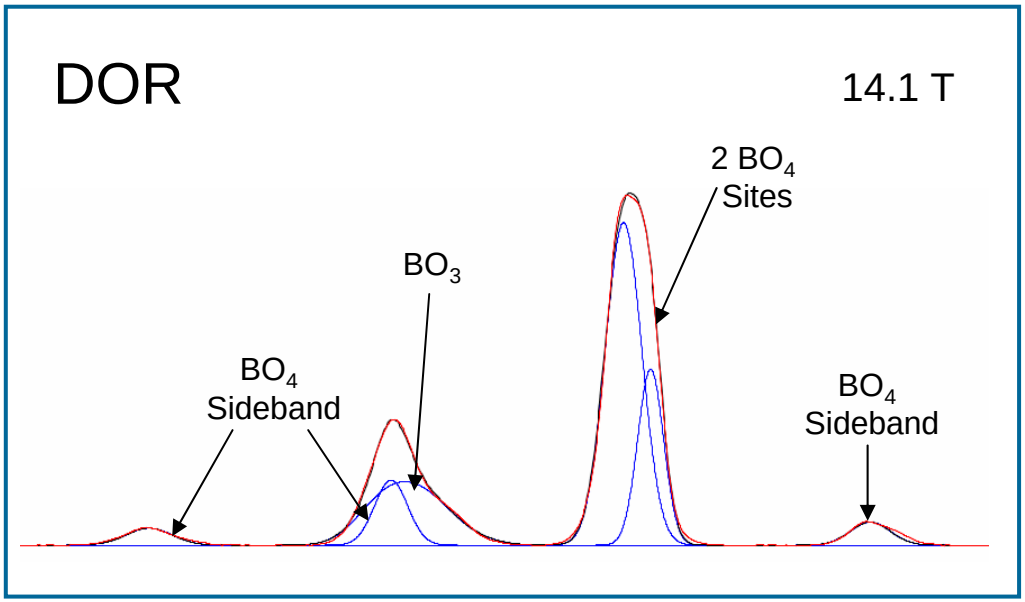
Base glass: contains
no bismuth or zinc

14.1 T

13.9 kHz





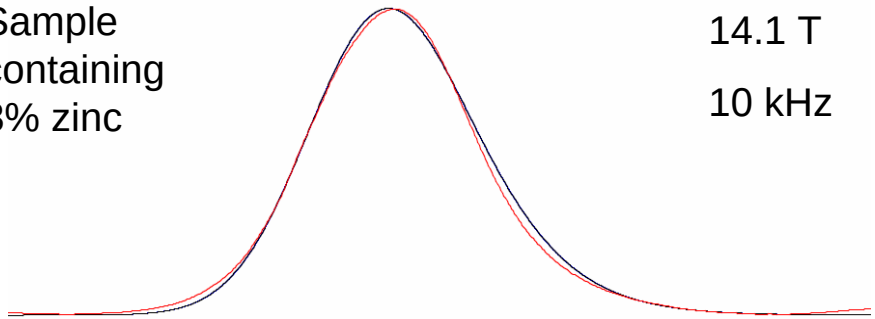


Model Samples – ^{23}Na

Sample containing 3% zinc

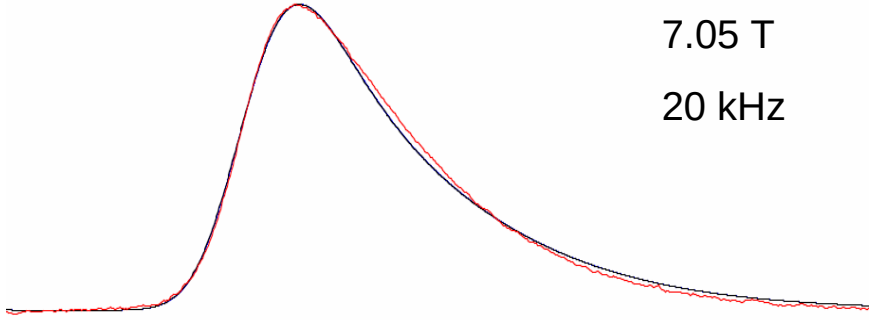
14.1 T

10 kHz

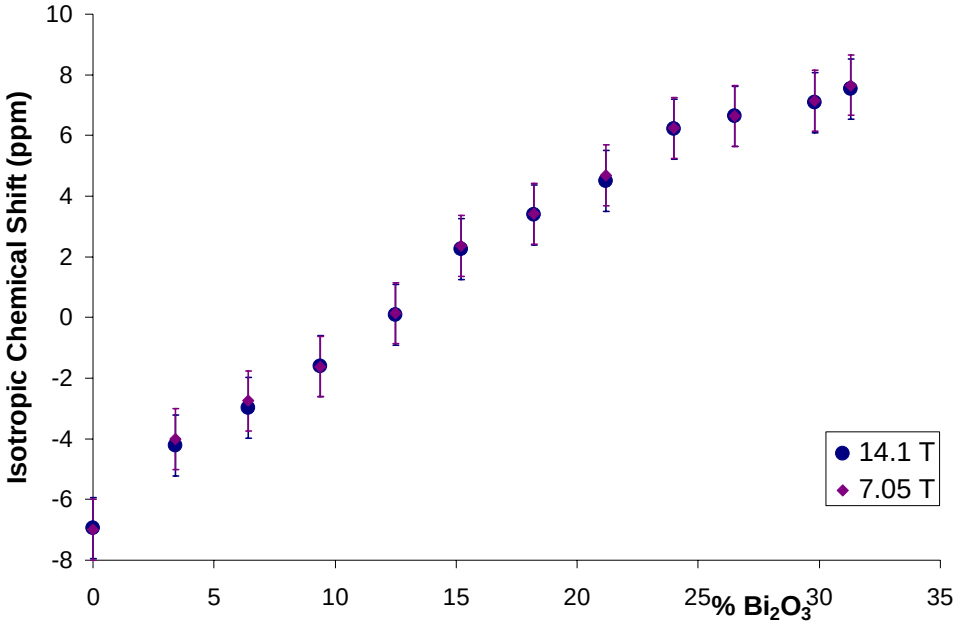


7.05 T

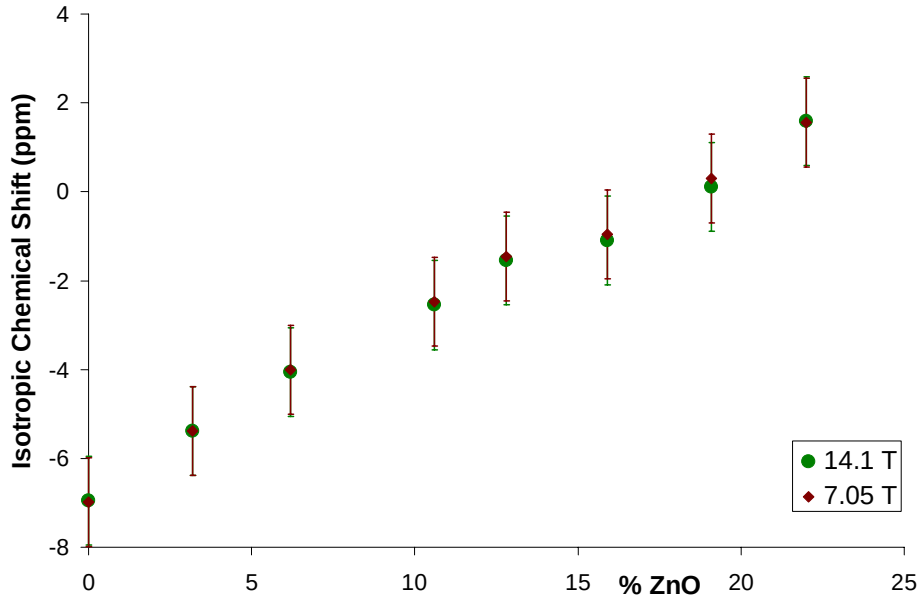
20 kHz



Bismuth Samples

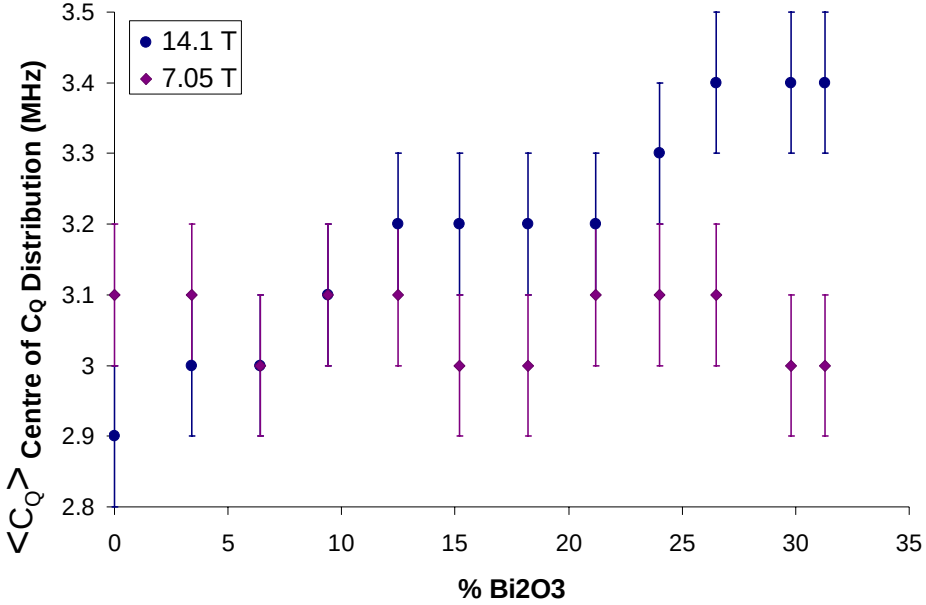


Zinc Samples

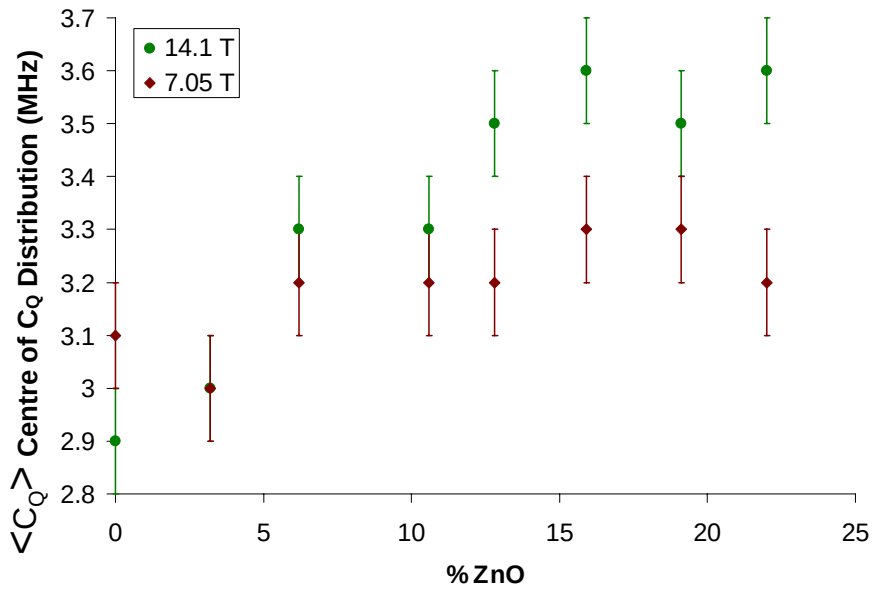


Model Samples – ^{23}Na

Bismuth Samples



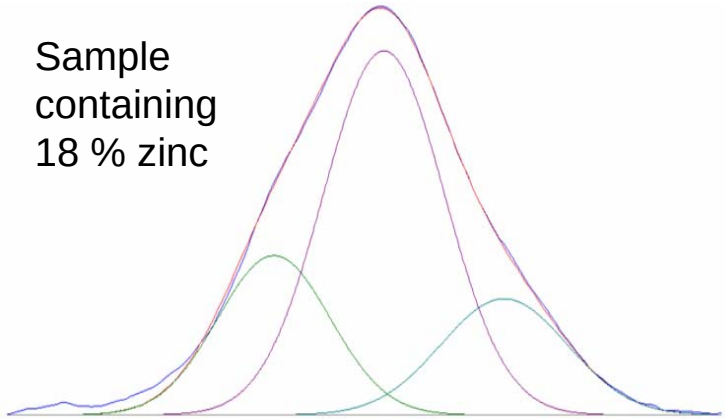
Zinc Samples

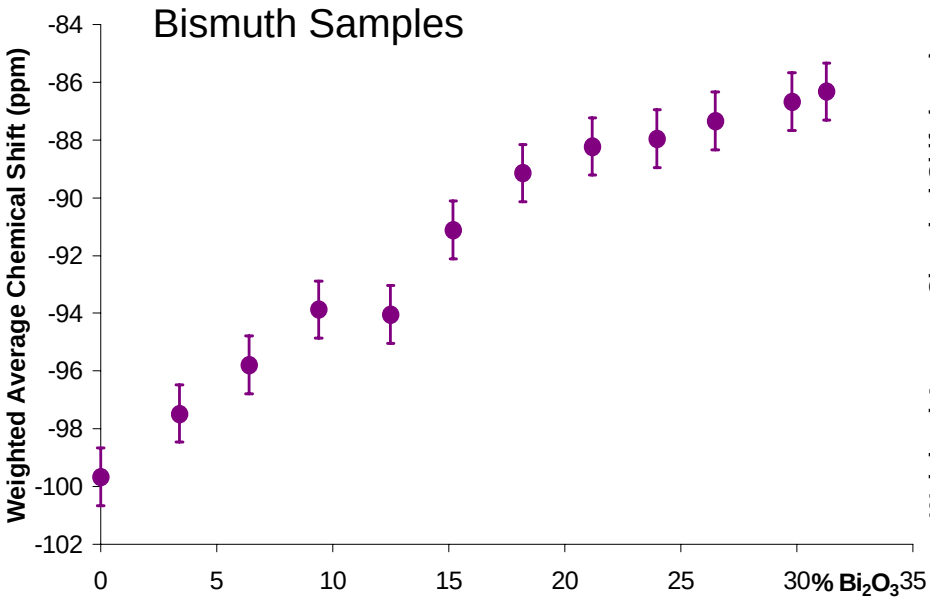


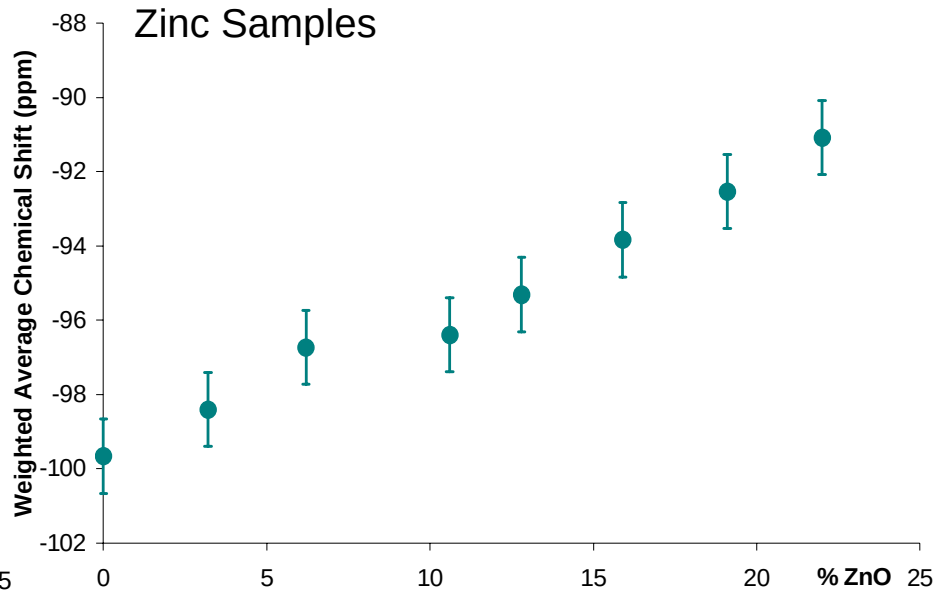
Model Samples – ^{29}Si

Predicted Q species:
- Q0 or Q1 at ~ – 83 ppm
- Q1 or Q2 at ~ – 93 ppm
- Q3 at ~ – 104 ppm

Sample containing 18 % zinc







Model Samples – Conclusions

Roles of bismuth and zinc:

- ^{11}B – Bi and Zn not replacing B in the network
- ^{23}Na – Bi and Zn acting as network modifiers
- ^{29}Si – Network becomes less connected with higher Bi or Zn content

Further work:

- 2D ^{29}Si – need enriched samples
- Samples with both bismuth and zinc

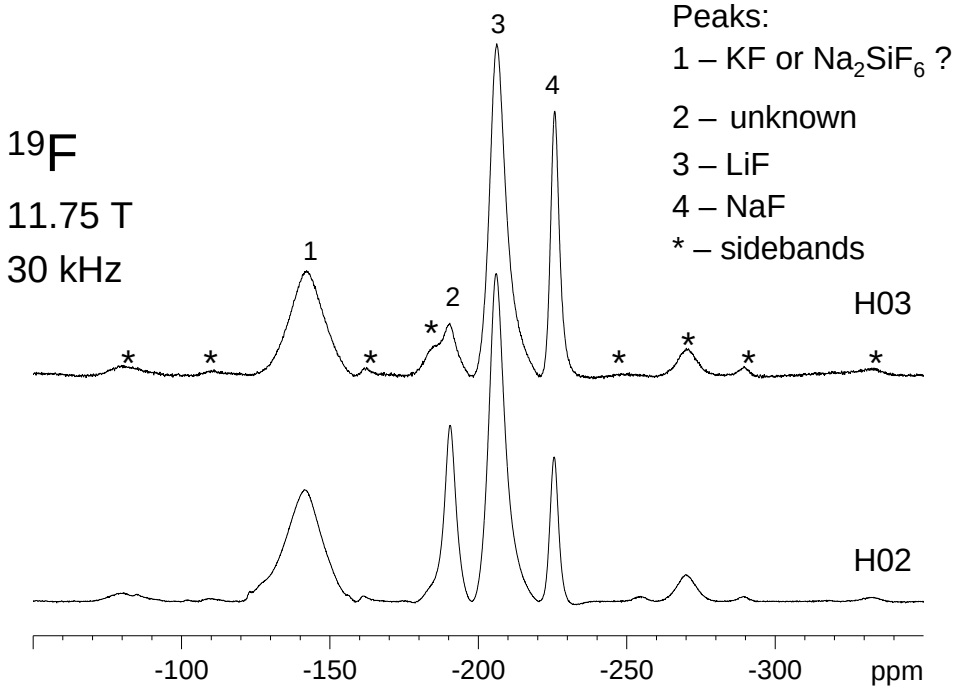
Fluorinated Glass Samples

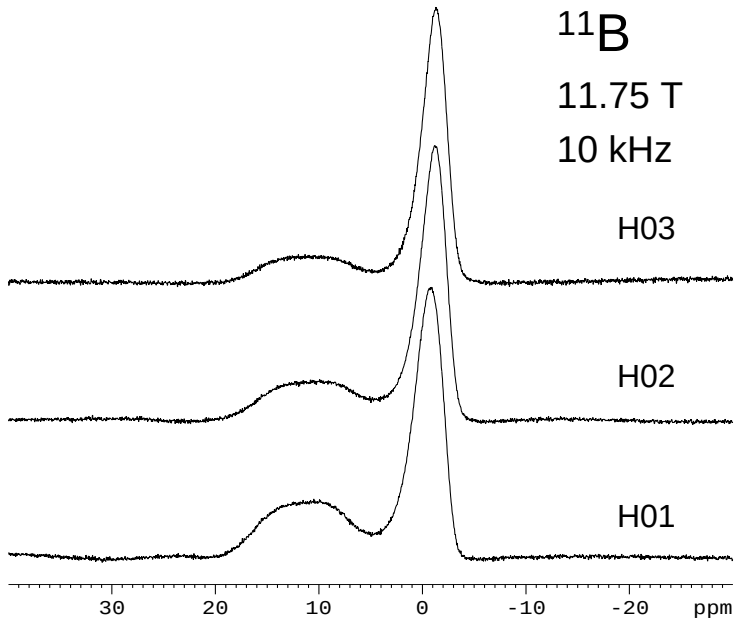
Samples:

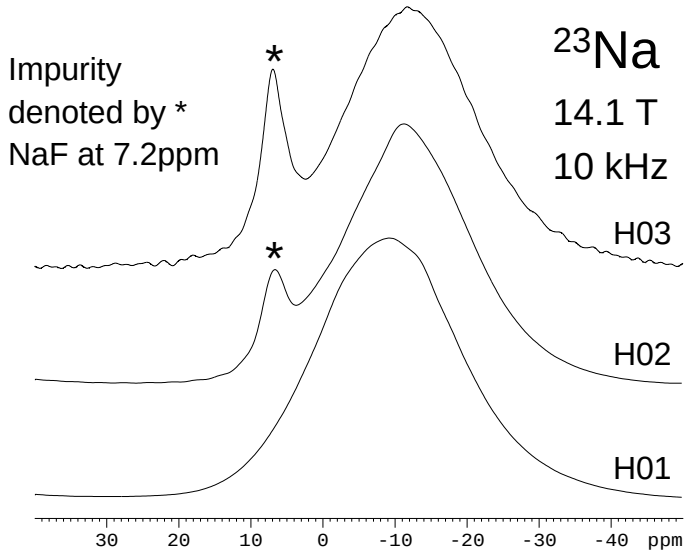
H01 – 0 mol% F

H02 – 5 mol% F

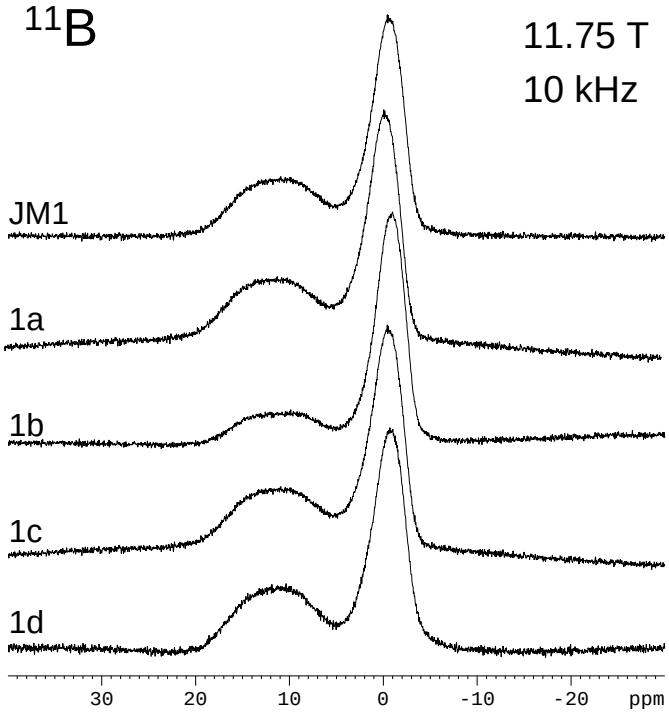
H03 – 10 mol% F

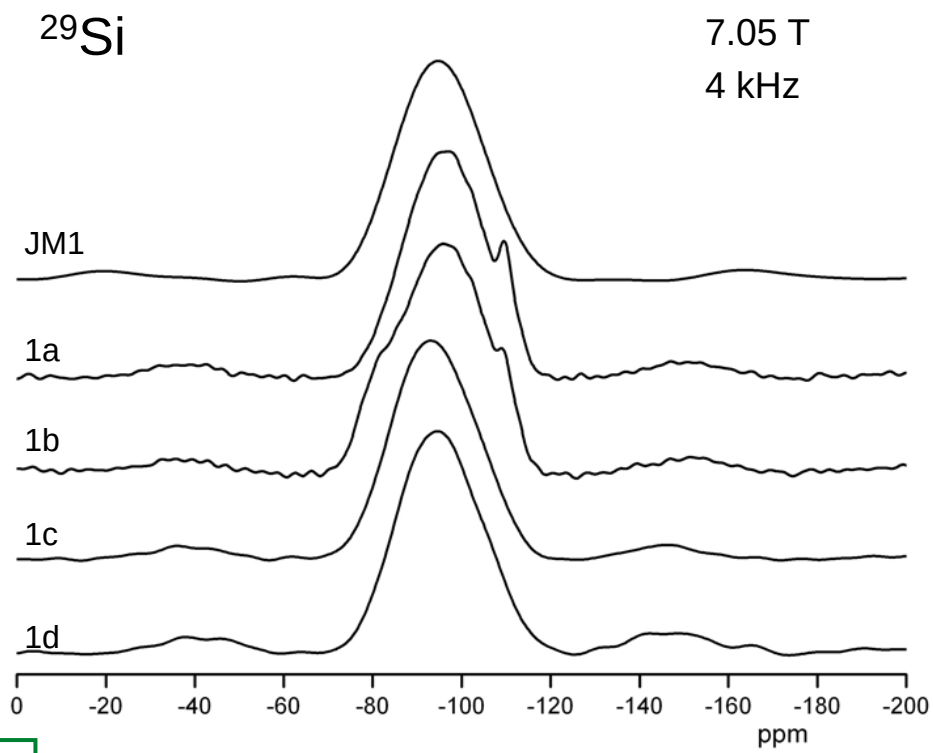






Crystallising Samples





JM1 – commercial

1a – heat treated

1b – heat treated and seeded

1c – no iron

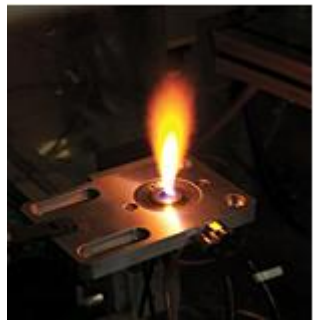
1d – JM1 made on small scale

Crystalline phases:

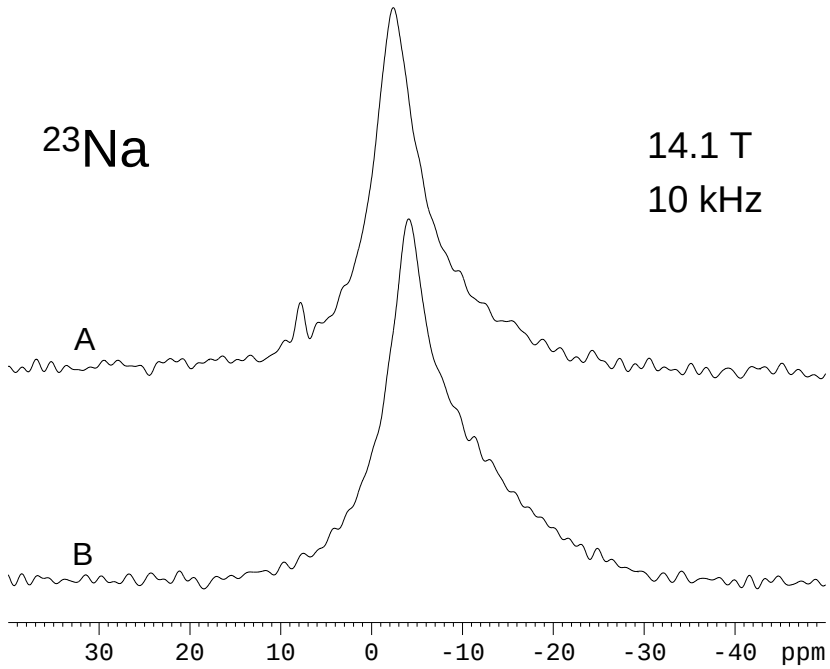
- Bi_2SiO_5 Bismuth monosilicate
- Eulytite $Bi_4(SiO_4)_3$

Flame Spray Pyrolysis

- Produces nanoparticles
- One-step process
- Investigate effect on structure



A - soda-lime
B - borosilicate



Acknowledgments

- Supervisors
  - Mark E. Smith, John V. Hanna
- Industrial Supervisors
  - Peter Bishop, Jon Booth, Hong Zheng
- NMR Group
  - Nathan Barrow, Andy Howes

THE UNIVERSITY OF WARWICK

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EPSRC
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Thank you for listening