Solid State NMR Characterisation of Zinc and Bismuth in Borosilicate Glasses

The Structure of Automotive Obscuration Enamels

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Contents

- Background – Automotive Enamels
  – Structure of Glasses
  – NMR
- Model Glasses – Aim
  – NMR results
  – Further Work

Background

Automotive Obscuration Enamels

Functions

- shield glue from UV light
- hide silver connections
- control of crystallisation to aid manufacturing
- aesthetic design

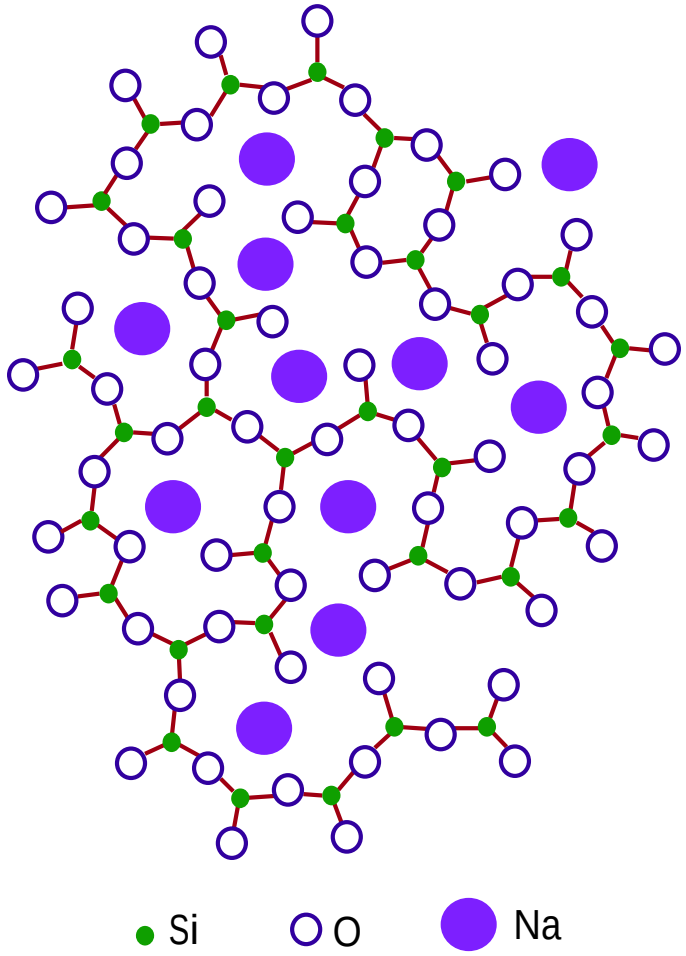
New Product

- must pass strict industry acid tests
- low firing temp. < 600 C
- control of thermal expansion

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



Sodium silicate

Borosilicate Glasses

- Zinc and bismuth added for physical properties
  - NMR literature: alkali borosilicates without these additions
- Effects of zinc and bismuth on the structure
- Commercial samples: no compositional trends
- Zinc and bismuth substitute boron in the compositions
  - do they also substitute it in the glass network?

Solid State NMR

- NMR: local structure
- Magic Angle Spinning: 54.74 → narrow spectra
  - Using 4 → 30 kHz
- NMR Isotropic Chemical Shift δ
- NMR on Quadrupolar nuclei: $I > {}^{1}/_{2}$
  - Looking at ^{11}B and ^{23}Na: spin $^{3}/_{2}$
  - Also ^{29}Si: spin $^{1}/_{2}$

Borosilicate Glasses

Compositions:

- Base Glass

  63% Si, 16% Na, 21% B
- B + Zn or Bi = 21 mol%
- Si + Na ~ constant for all samples
- Some contain more Zn and Bi than commercial glasses

NMR Experiments:

Basic: single pulse

^{11}B, ^{23}Na, ^{29}Si

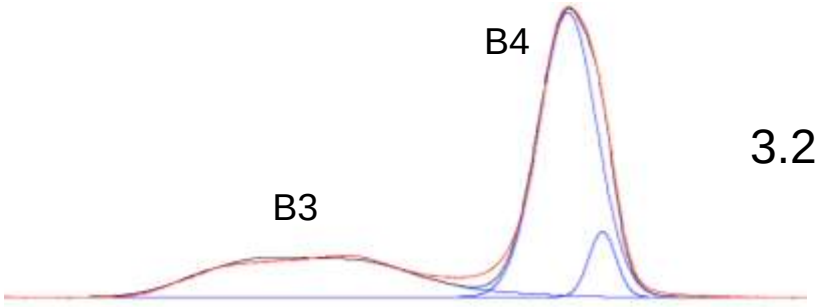
To improve resolution:

- ^{11}B Multiple Quantum Magic Angle Spinning (MQMAS)
- ^{11}B Double Rotation (DOR)

^{11}B NMR

11.7 T

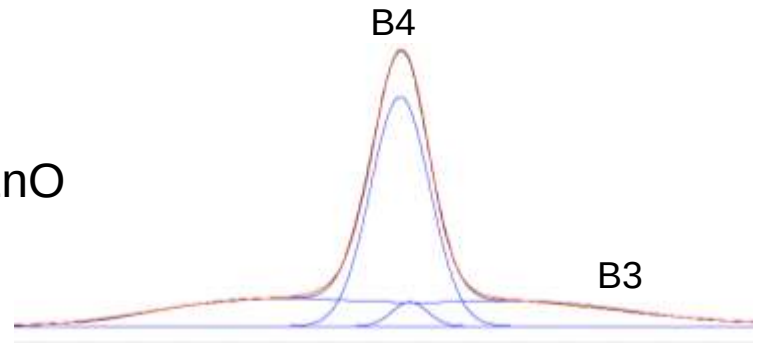
10 kHz

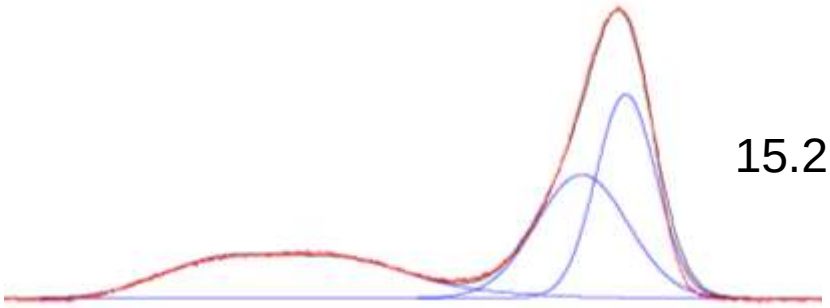


3.2 mol% ZnO

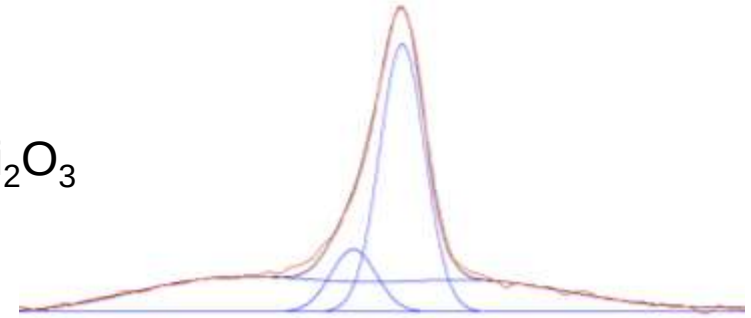
7.1 T

10 kHz



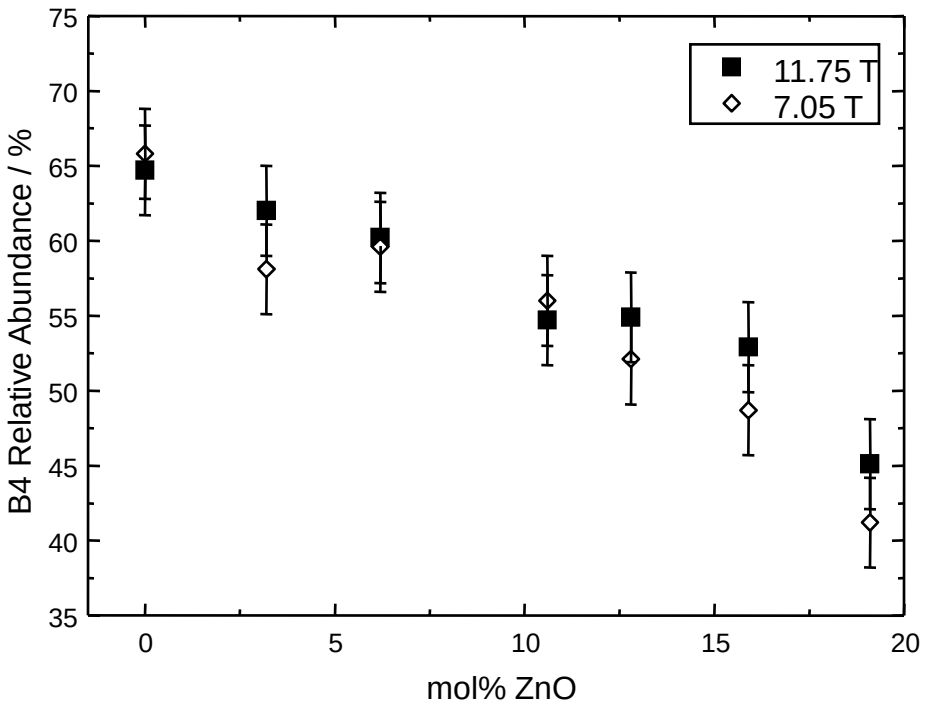


15.2 mol% Bi_2O_3

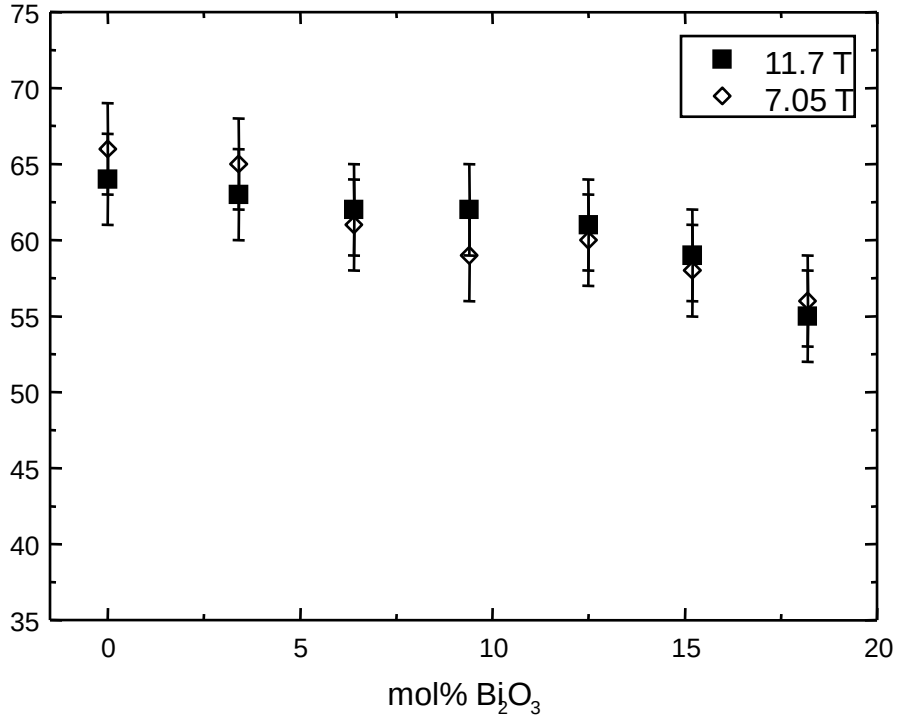


^{11}B NMR

Zinc

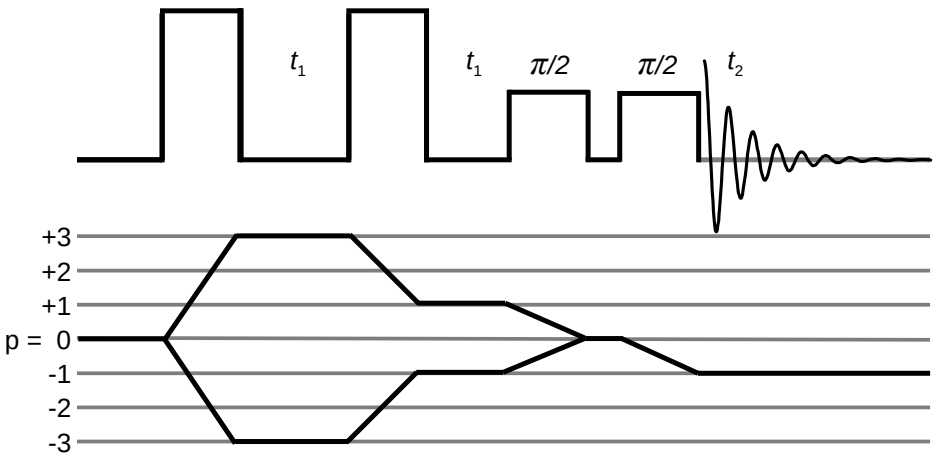


Bismuth



^{11}B – MQMAS

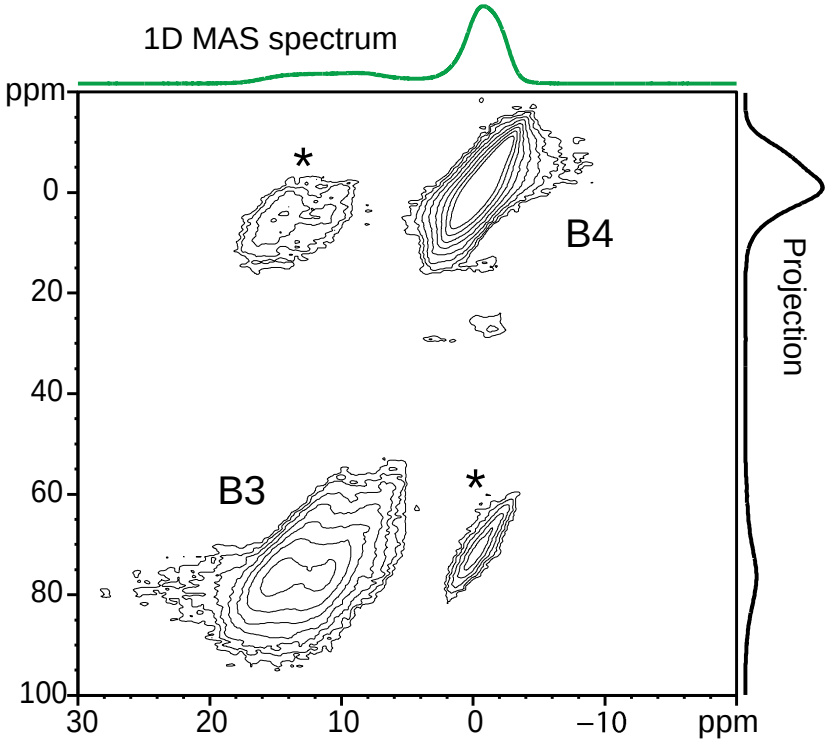
Multiple Quantum Magic Angle Spinning



Base glass

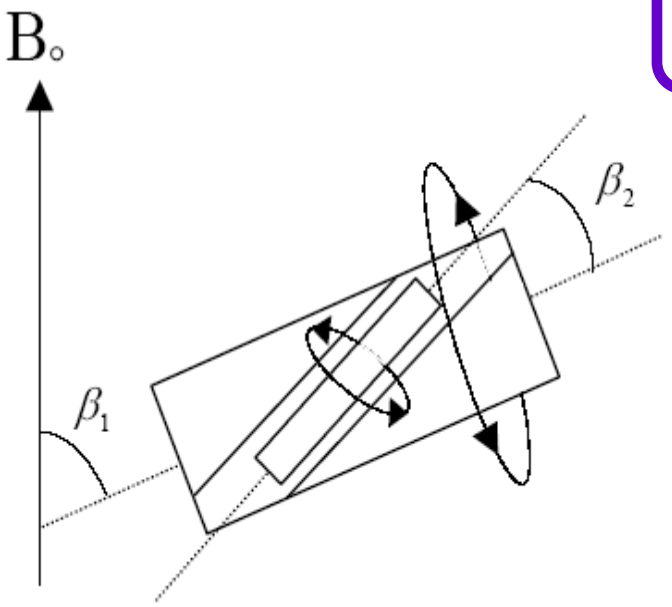
14.1 T

13.9 kHz



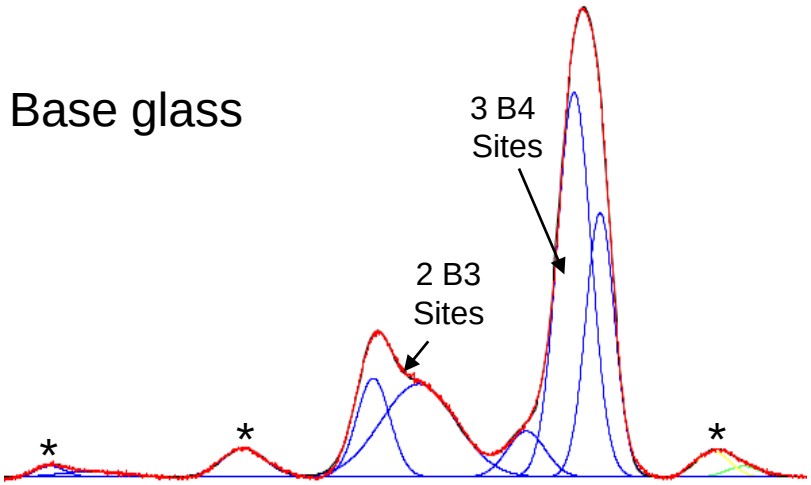
*spinning sideband

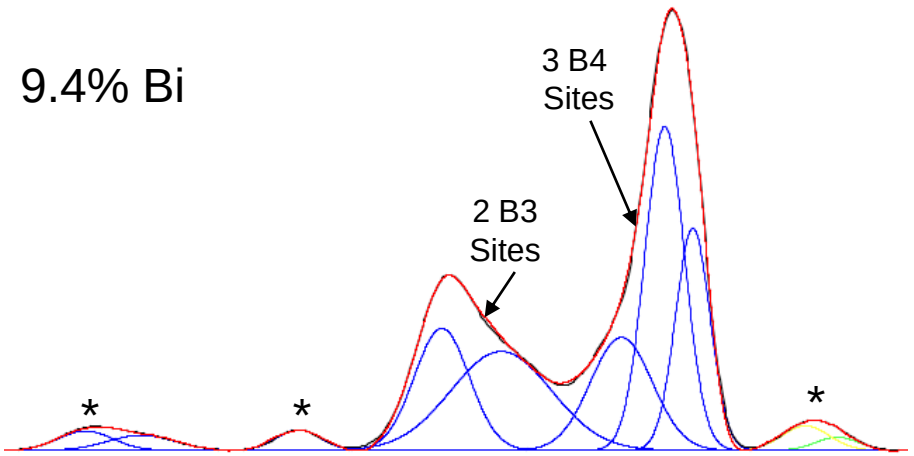
^{11}B – DOR



- More quantitive and sensitive than MQMAS
- Difficult to spin
- Eliminates line broadening

11.7 T





* denote spinning sidebands

^{23}Na NMR

Lines fitted in black

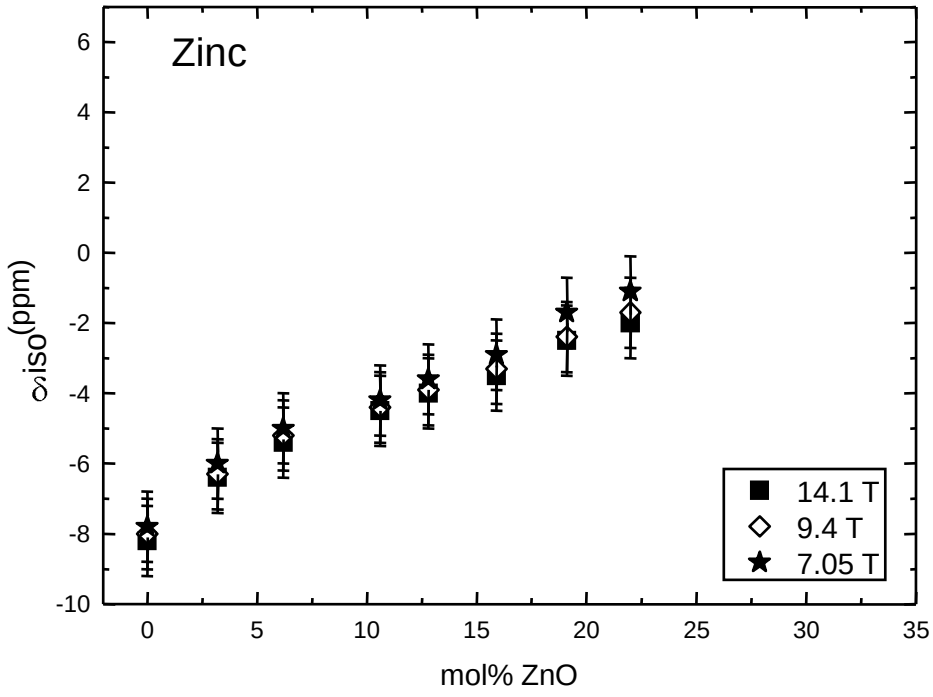
14.1 T

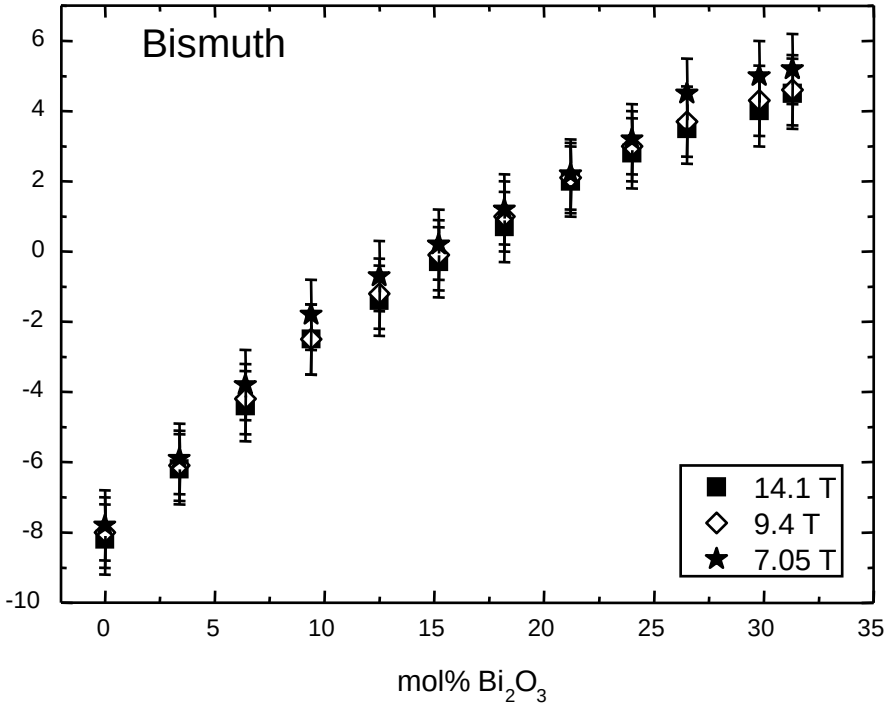
10 kHz

3.2 % Zinc

7.1 T

20 kHz





Increase in electron density → network becomes less connected

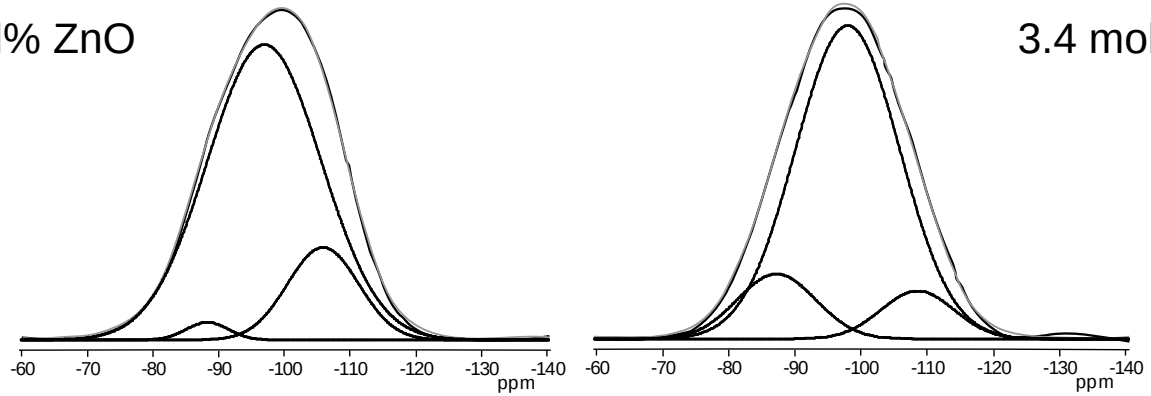
^{29}Si NMR

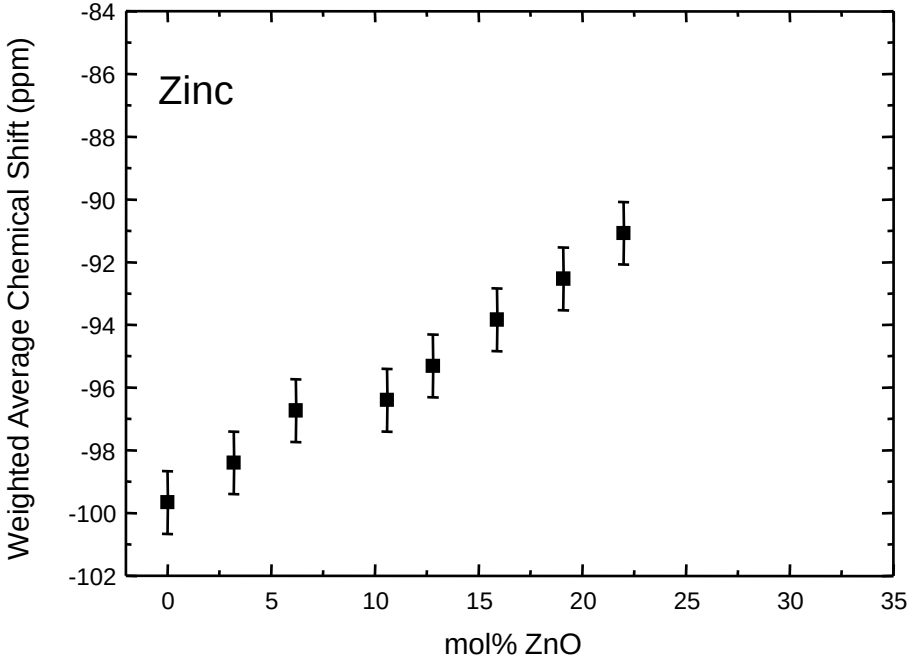
3.2 mol% ZnO

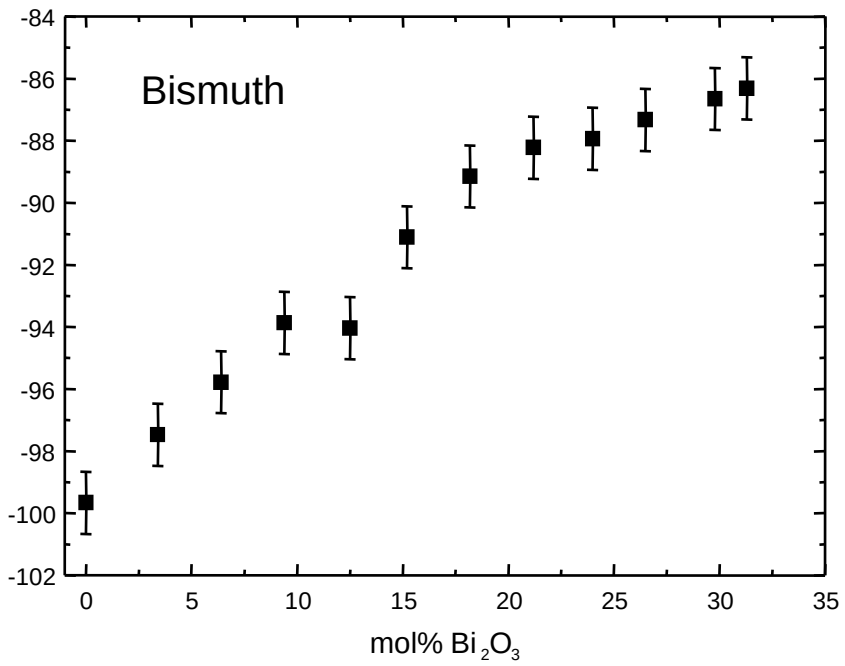
3.4 mol% Bi_2O_3

7.1 T

3.5 kHz







Nuclei less shielded → less bridging oxygens → less connected

Conclusions

- Roles of zinc and bismuth:
  - Bi and Zn not replacing B in the network
  - Network is less connected with higher Bi / Zn content
  - Bi and Zn acting as network modifiers
- Zinc and bismuth not acting identically
- Further work: zinc and bismuth together

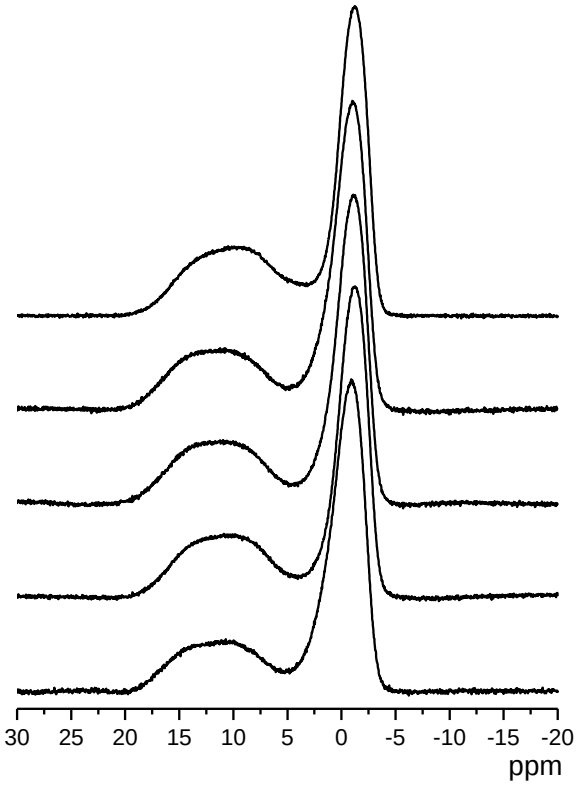
Zinc-Bismuth Glasses

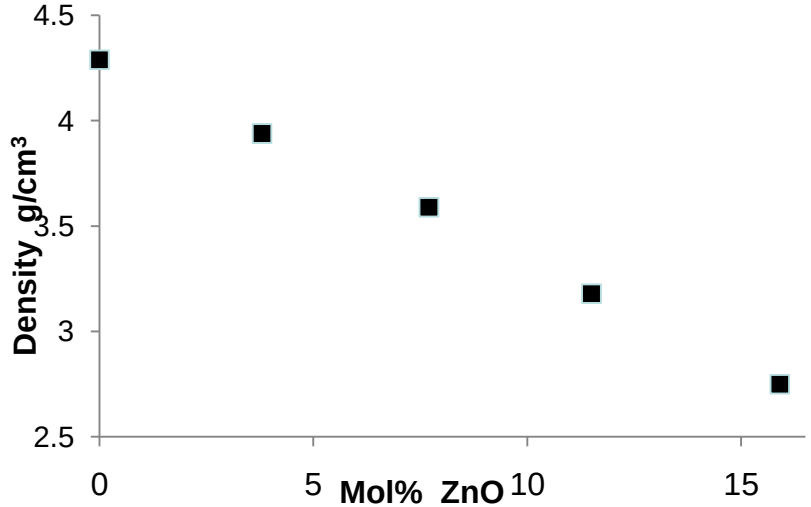
Mol%

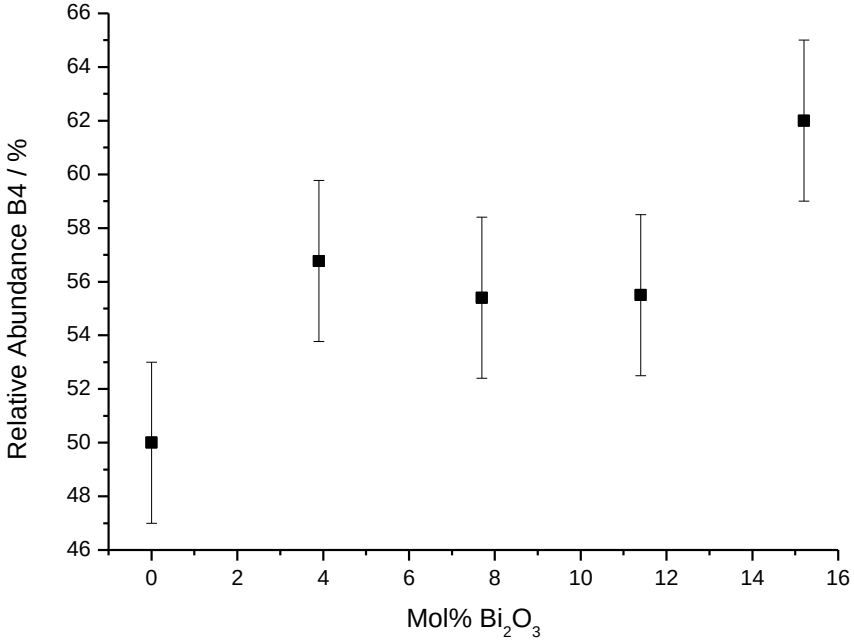
	SiO_2	B_2O_3	Na_2O	Bi_2O_3	ZnO
ZB1	64.1	6.1	14.3	15.2	0
ZB2	64.6	5.6	14.5	11.4	3.8
ZB3	64.2	5.7	14.7	7.7	7.7
ZB4	64.1	5.9	14.5	3.9	11.5
ZB5	62.8	5.9	15.3	0	15.9

^{11}B

11.7 T







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Thank you for listening