Borate glasses

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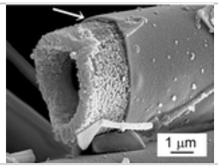
BORATES – TECHNOLOGICAL INTEREST

Since 1915

Glass with thermal shock resistance (Pyrex)

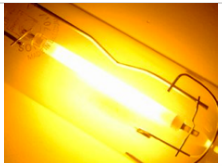
borosilicate glasses



Since 60's

Bioactive glasses as implant materials

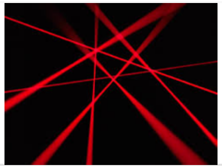
Na-K-Ca borate glasses



Since 70's

High-pressure sodium vapor lamp

Alumino-borate glasses



Since 70's

Non-linear optical borate crystals

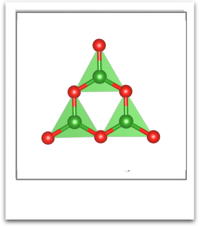
Alkali-, Rare-Earth- borates

Now

Potential solid electrolytes and cathode materials

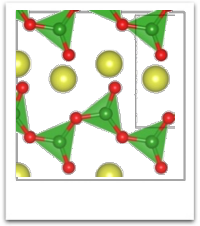
Alkali-borates with transition elements

OUTLINE



B_2O_3 glass

Archetypal glass former

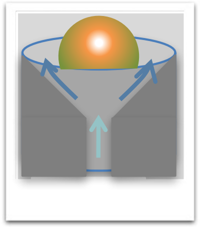


Alkali borate glasses (Li, Na, K, Rb, Cs)

Vitrification domains

Alkali effects on physical properties

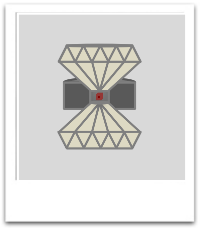
Glass structure: short- and intermediate-range order



From glass to melt

Structure of alkali borate melts

Depolymerization of the borate network



Polyamorphism

B_2O_3 vs SIO_2

- An important advantage of borate glasses over silica glasses is their significantly lower melting temperature

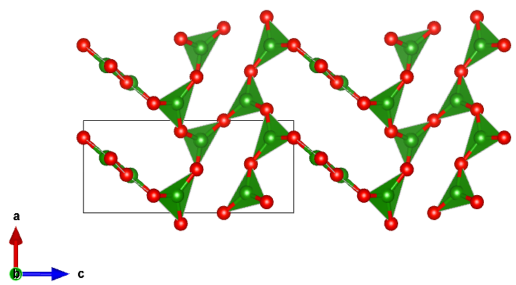
	B_2O_3	SiO_2
Average network connectivity	3	4
Mass Density	1.844 g.cm^{-3}	2.202 g.cm^{-3}
T_g	260°C	1100°C
T_m	450°C	1728°C
Liquid viscosity (log η at 1200°C)	1.66 P	12.6 P
chemical durability	low	high
Thermal expansion (α)	161.6 × 10^{-7} K^{-1}	5.35 × 10^{-7} K^{-1}

- Used in combination with other oxides such as Al_2O_3 or SiO_2, this leads to:
  - improve chemical durability,
  - decrease melting temperatures.

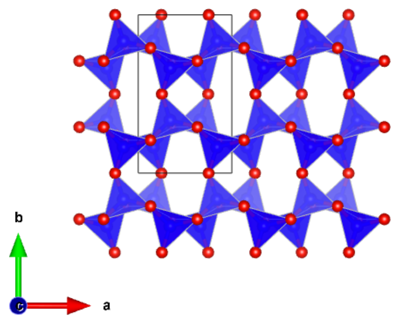
PECULIARITIES OF B_2O_3

- B_2O_3 does not crystallize at ambient pressure : « *ideal glass former* »
- But two polymorphs of B_2O_3 can be formed when pressure is applied

B_2O_3 – I
low-pressure phase (< 2 GPa)



B_2O_3 – II
high-pressure phase

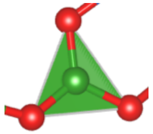


d(v-B_2O_3) = 1.84 g.cm^{-3} << d(B_2O_3 – I)=2.55 g.cm^{-3}

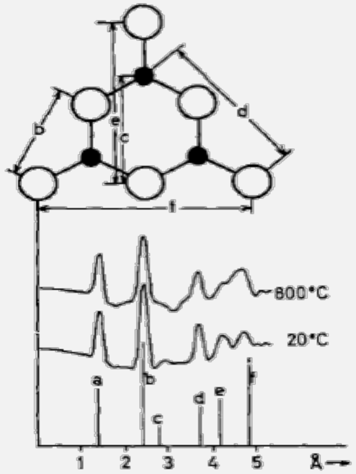
→ *Why the glass structure is less compact ?*

PECULIARITIES OF B_2O_3

- Glassy B_2O_3 is solely constituted by BO_3 units

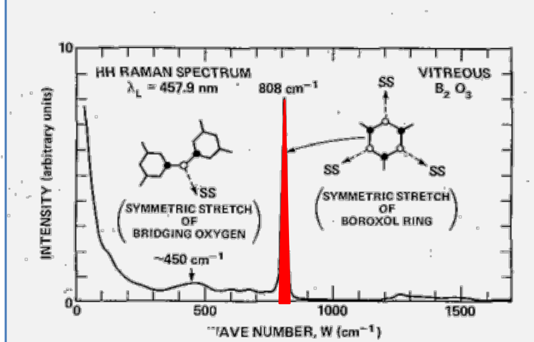


X-ray diffraction



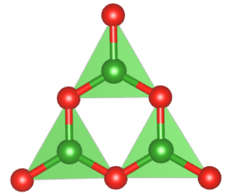
Krogh-Moe *et al.* JNCS 1969

Raman



Galeener et al. J. Phys. 1982

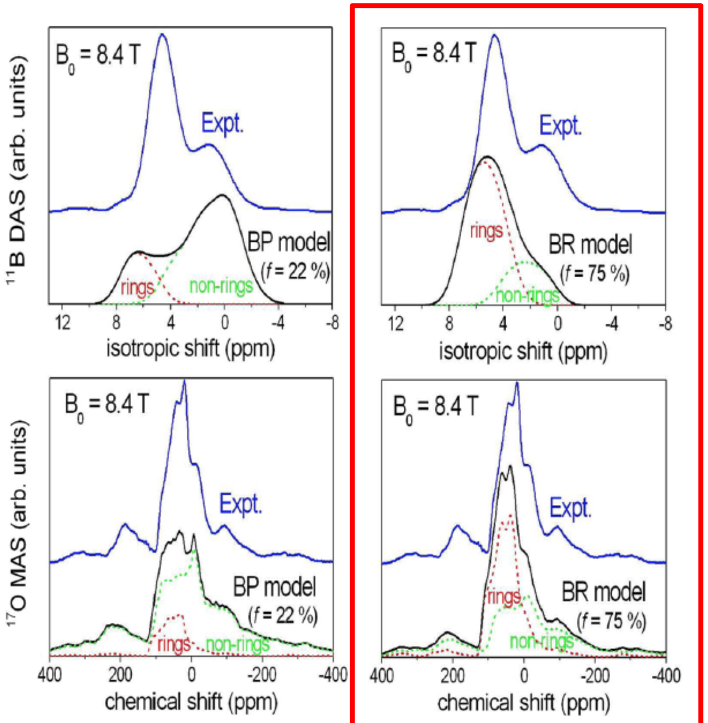
Boroxol rings (B_3O_6)



Existence of an intermediate range order in glass …

PROPORTION OF BOROXOLS IN V-B_2O_3 ?

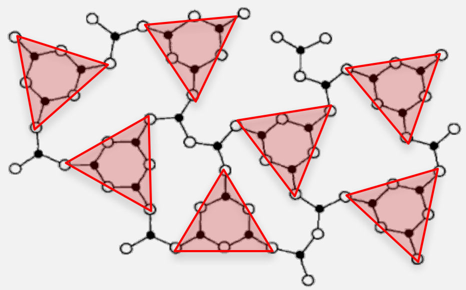
[11]B and [17]O NMR



22%
boroxol rings

75%
boroxol rings

~75% of boroxol rings in B_2O_3 glass



Krogh-Moe JNCS 1969 / Ferlat PRL 2008

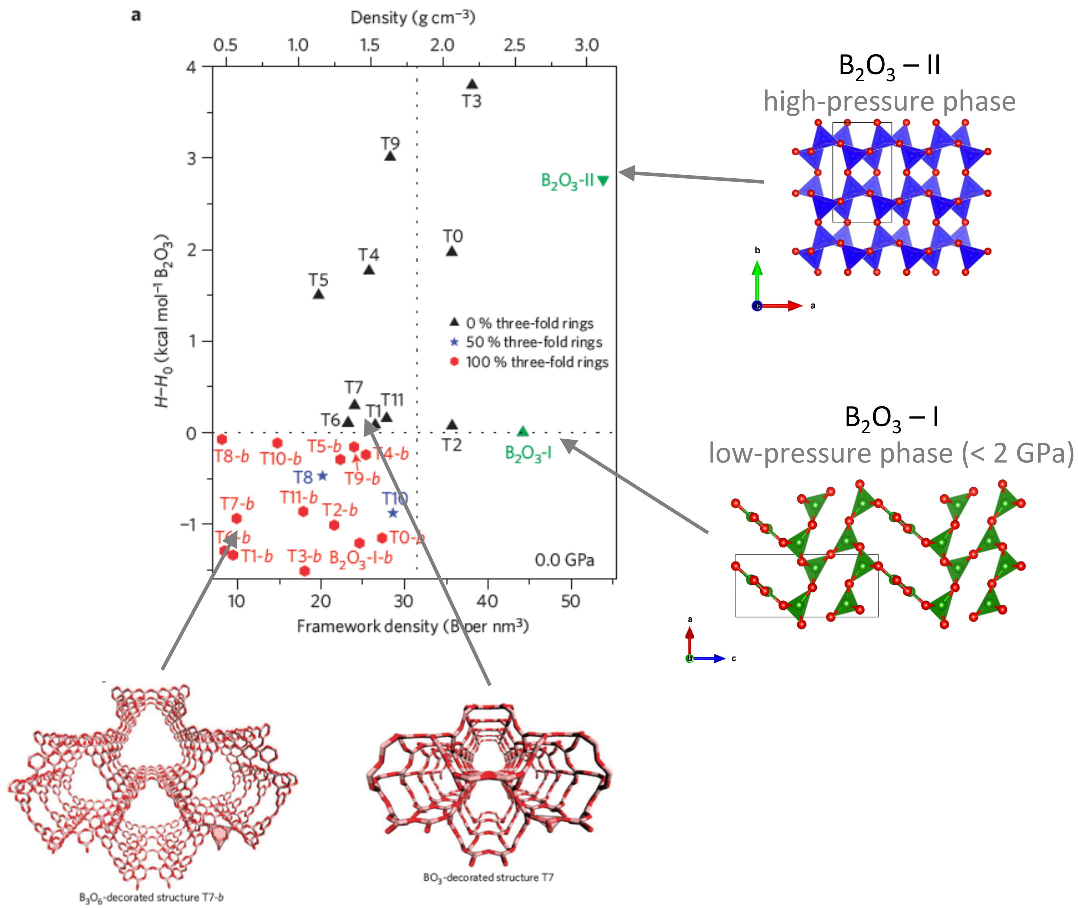
Ferlat PRL 2008

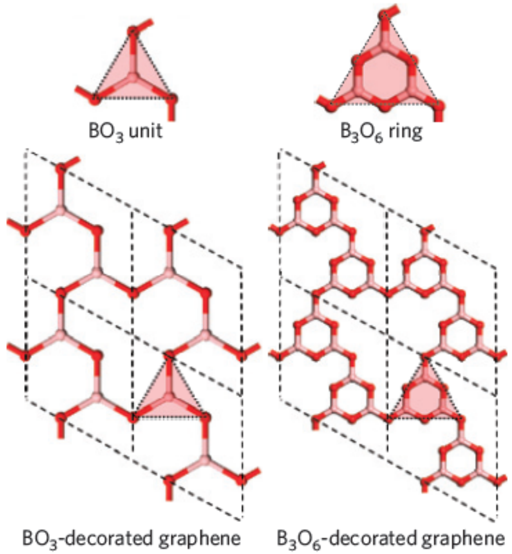
Why B_2O_3 does not crystallize at ambient pressure ?

PECULIARITIES OF B_2O_3

- Predictions of crystalline B_2O_3 forms

Ambient pressure



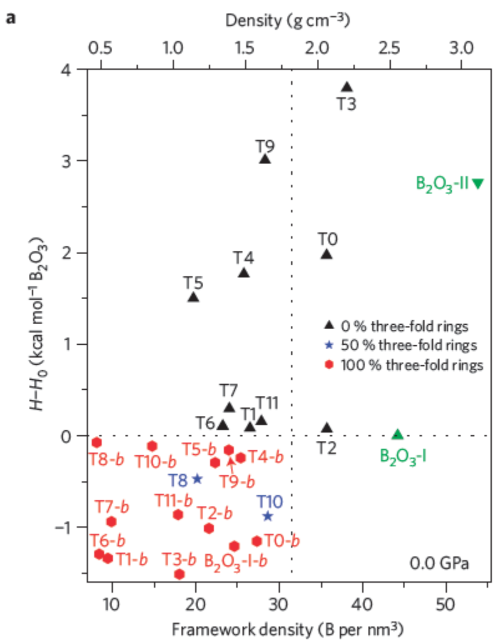


Ferlat et al. Nat. Mater. 2012

PECULIARITIES OF B_2O_3

- Predictions of crystalline B_2O_3 forms

Ambient pressure



At ambient pressure, the crystallization is avoided as a result of the existence of several competing phases that eventually induces the system amorphization.

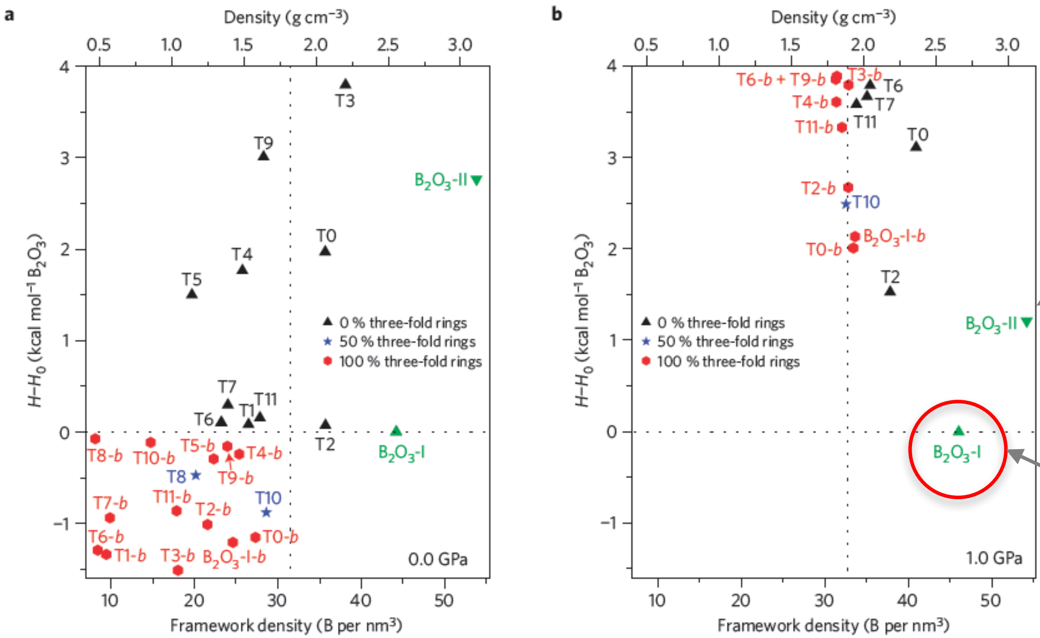
Ferlat et al. Nat. Mater. 2012

Peculiarities of B_2O_3

- Predictions of crystalline B_2O_3 forms

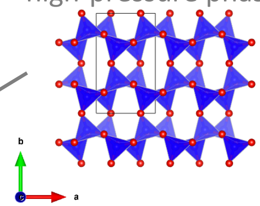
Ambient pressure

1 GPa



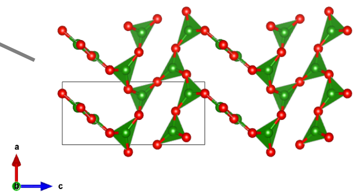
B_2O_3 – II

high-pressure phase



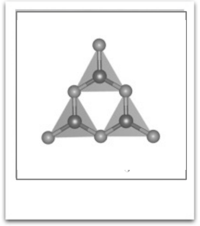
B_2O_3 – I

low-pressure phase (< 2 GPa)



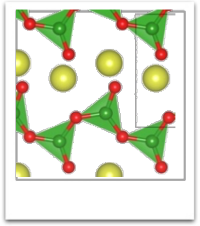
Ferlat et al. Nat. Mater. 2012

OUTLINE



B_2O_3 glass

Archetypal glass former



Alkali borate glasses (Li, Na, K, Rb, Cs)

Vitrification domains

Alkali effects on physical properties

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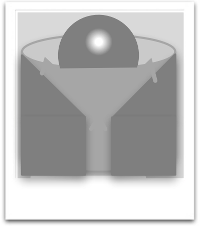
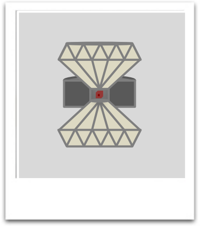


From glass to melt

Structure of alkali borate melts

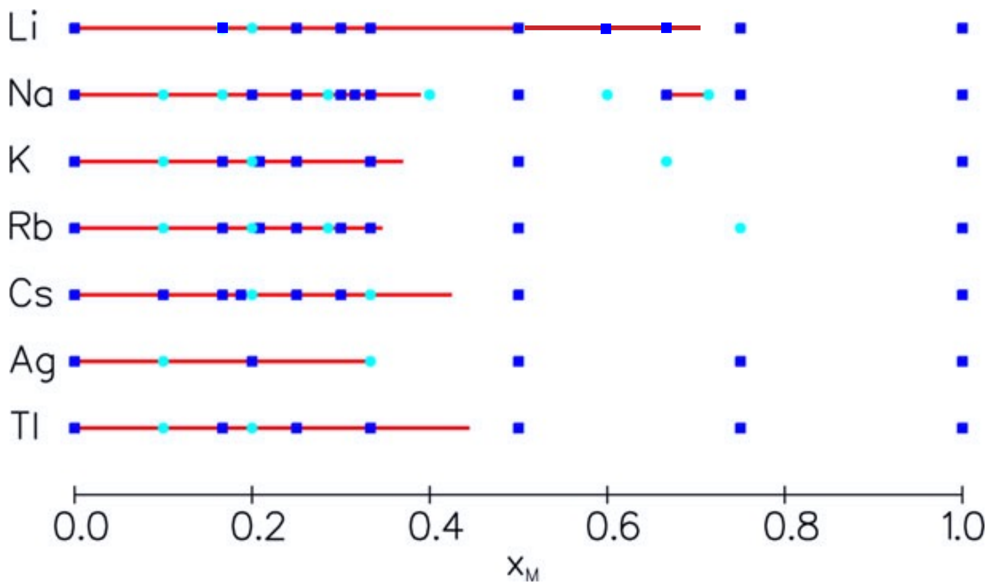
Depolymerization of the borate network



Polyamorphism

ALKALI BORATE: VITRIFICATION DOMAINS

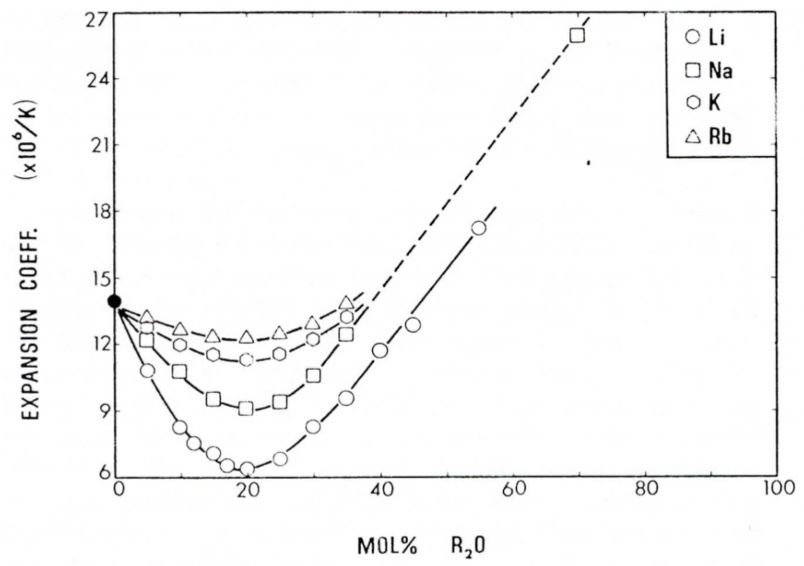
- A large composition range:

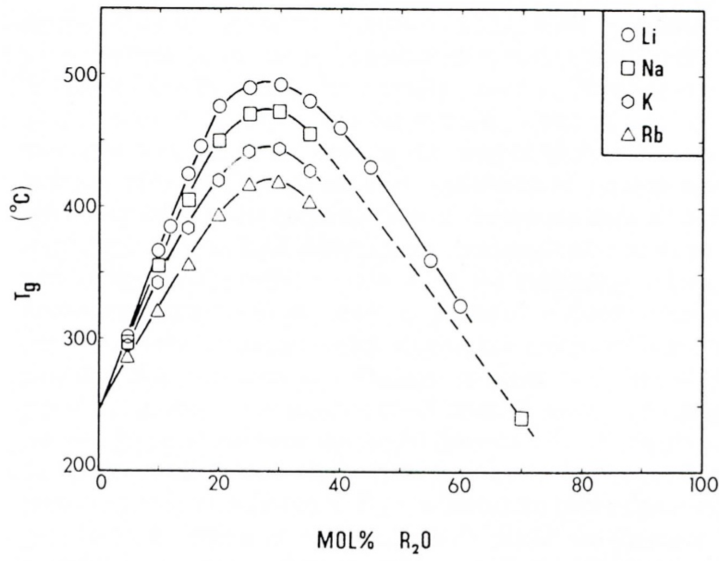


- crystalline phase with unknown structures
- crystalline phase with known structures
- glass forming region

Wright et al. PCG. 2015

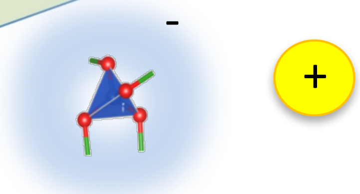
Borate anomalies





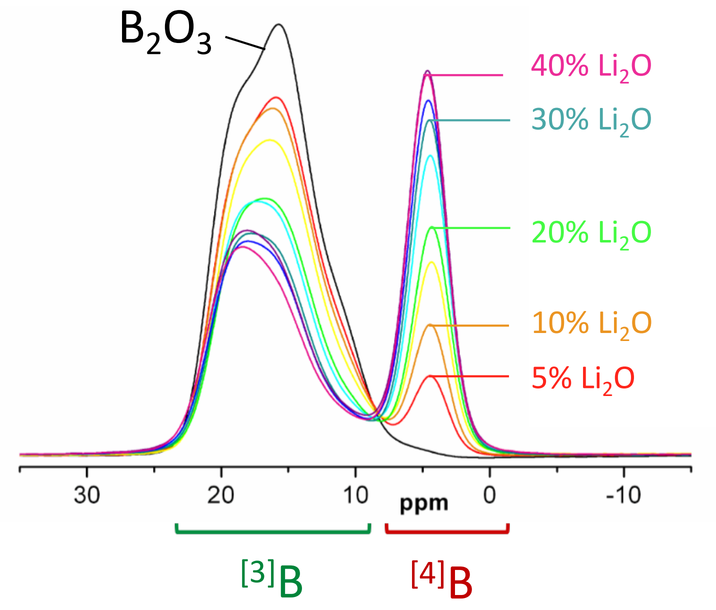
Shelby *et al. J. Am. Ceram. Soc.* 66, 225 (1982)

What happens when we add alkalis ?

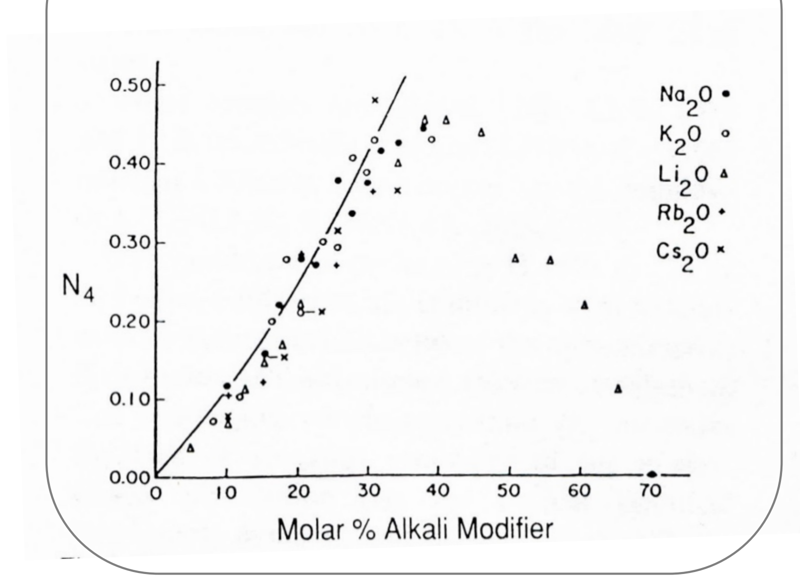


- By adding alkali oxide into B_2O_3 : [3]B ⟶ [4]B conversion

[11]B NMR



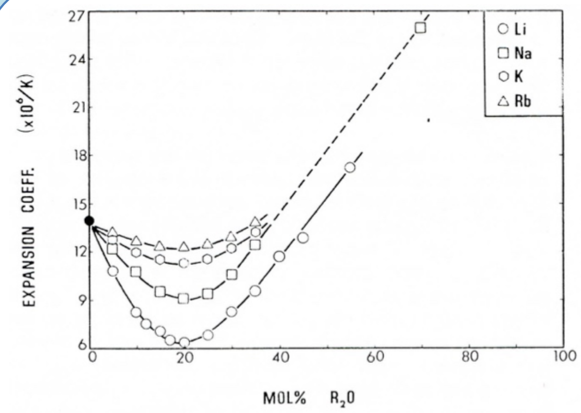
Proportion of [4]B

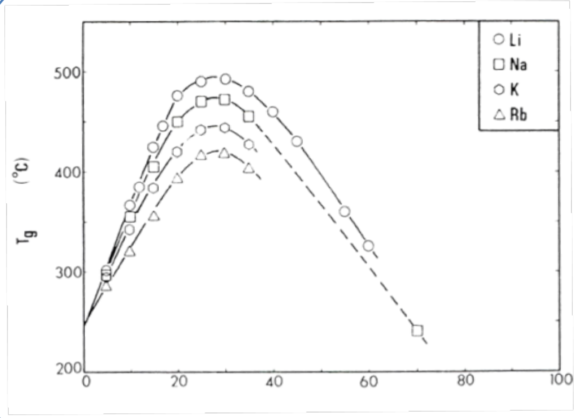


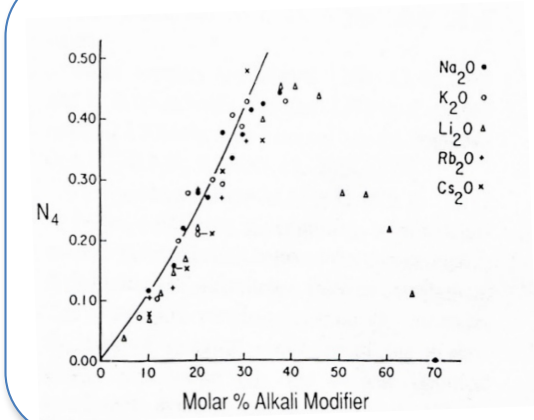
N. Barrow – Ph-D thesis - 2006

Bray and O'Keefe – PCG (1963)
Zhong et al. JNCS 111, 67 (1989)

RELATION N_4 AND THE ANOMALIES ?



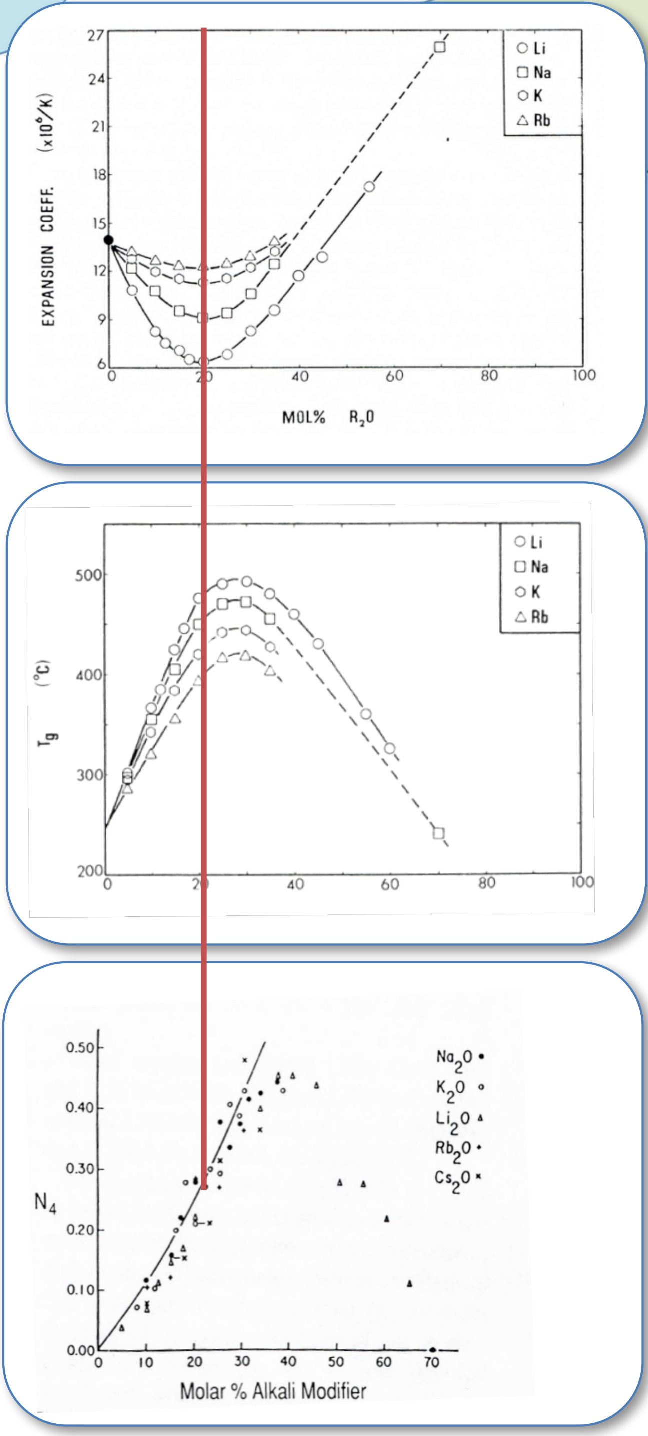




Zhong et al. JNCS 111, 67 (1989) / Shelby *et al. J. Am. Ceram. Soc.* 66, 225 (1982)

RELATION N_4 AND THE ANOMALIES ?

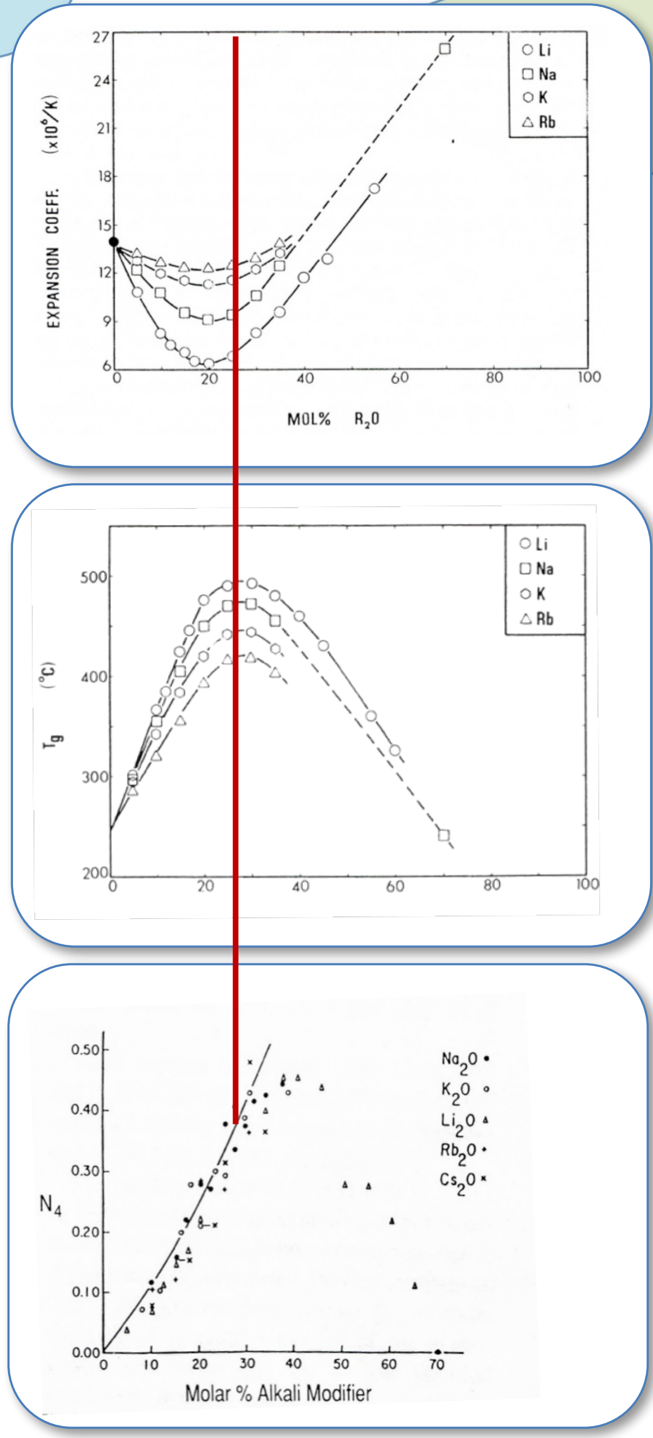
- Expansion coefficient minimum at 20mol%



Zhong et al. JNCS 111, 67 (1989) / Shelby *et al. J. Am. Ceram. Soc.* 66, 225 (1982)

Relation N_4 and the anomalies ?

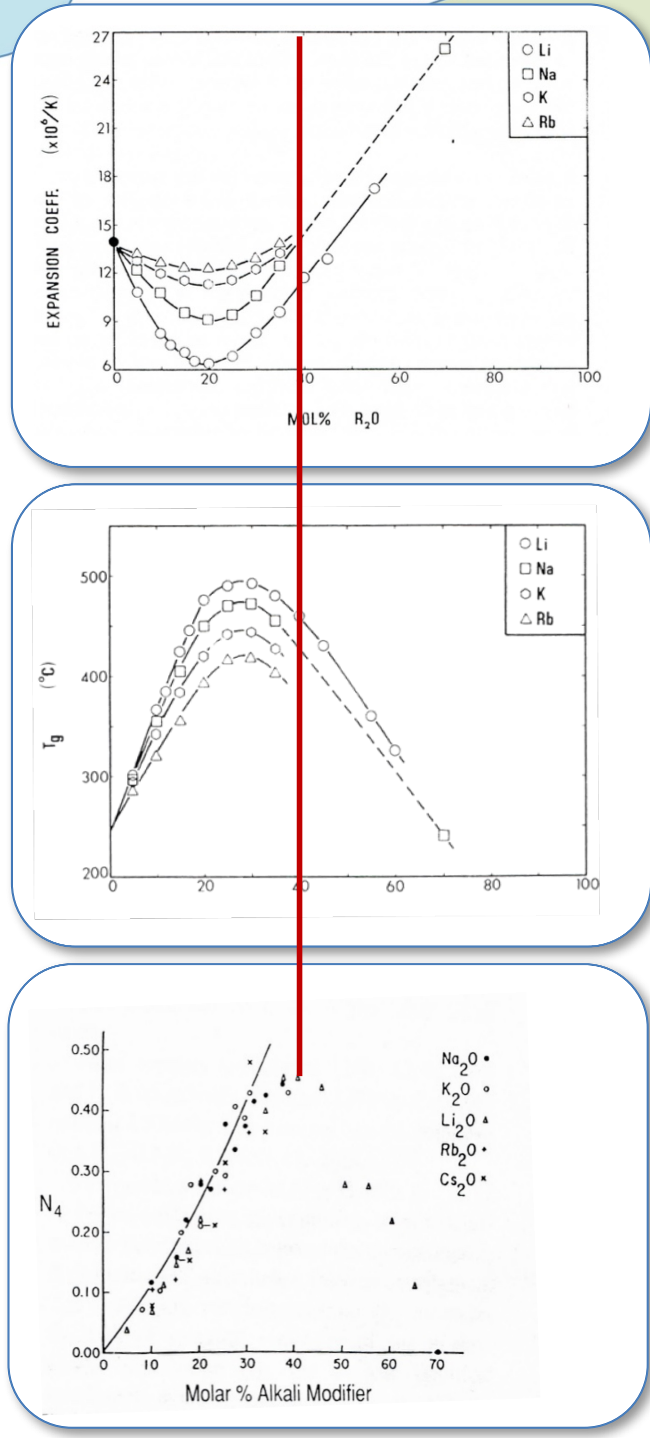
- Expansion coefficient minimum at 20mol%
- Tg maximum at 27mol%



Zhong et al. JNCS 111, 67 (1989) / Shelby *et al. J. Am. Ceram. Soc.* 66, 225 (1982)

Relation N_4 and the anomalies ?

- Expansion coefficient minimum at 20mol%
- Tg maximum at 27mol%
- N4 maximum around 45mol%



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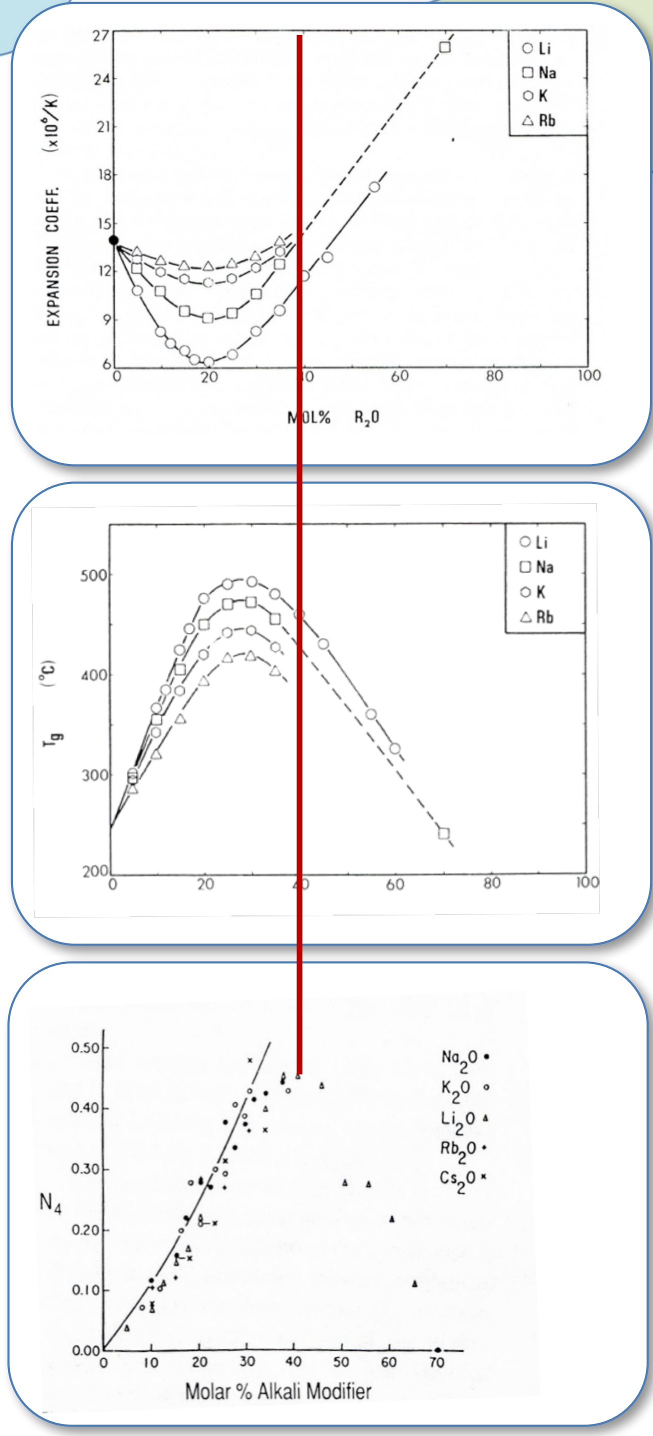
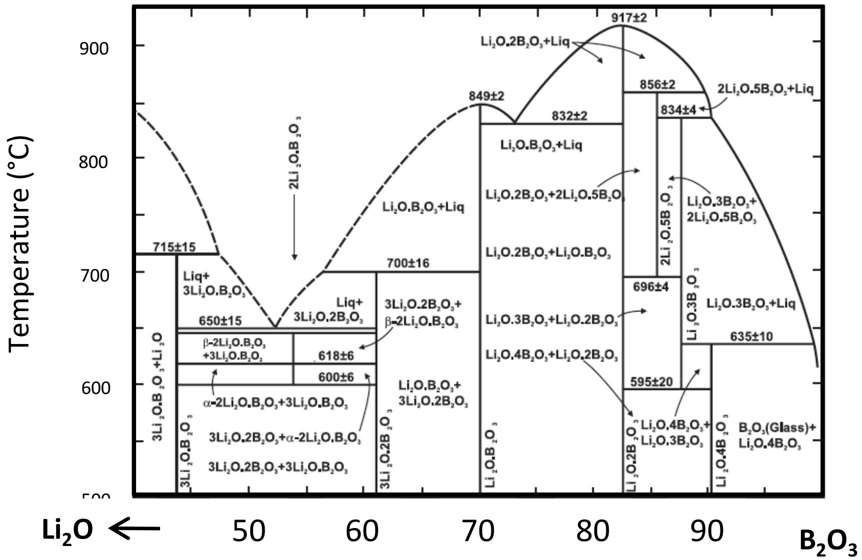


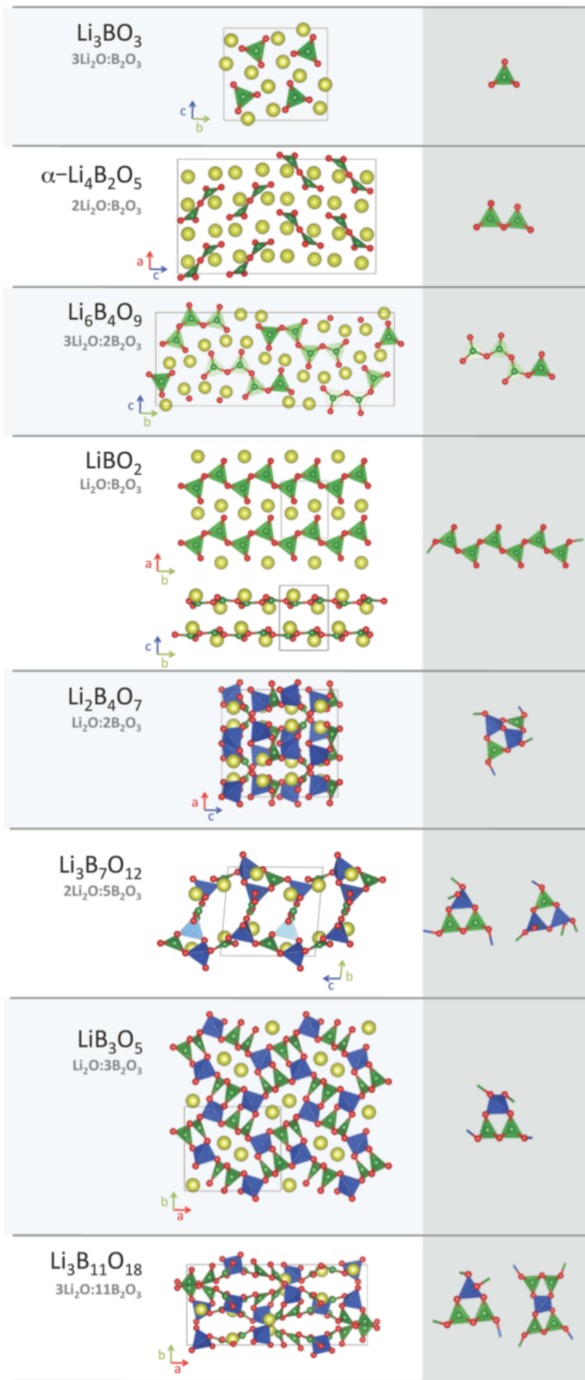
→ *The origin of these anomalies is not fully ascribable to the presence of [4]B…*

→ *Let's have a look at the crystalline samples…*

Zhong et al. JNCS 111, 67 (1989) / Shelby *et al. J. Am. Ceram. Soc.* 66, 225 (1982)

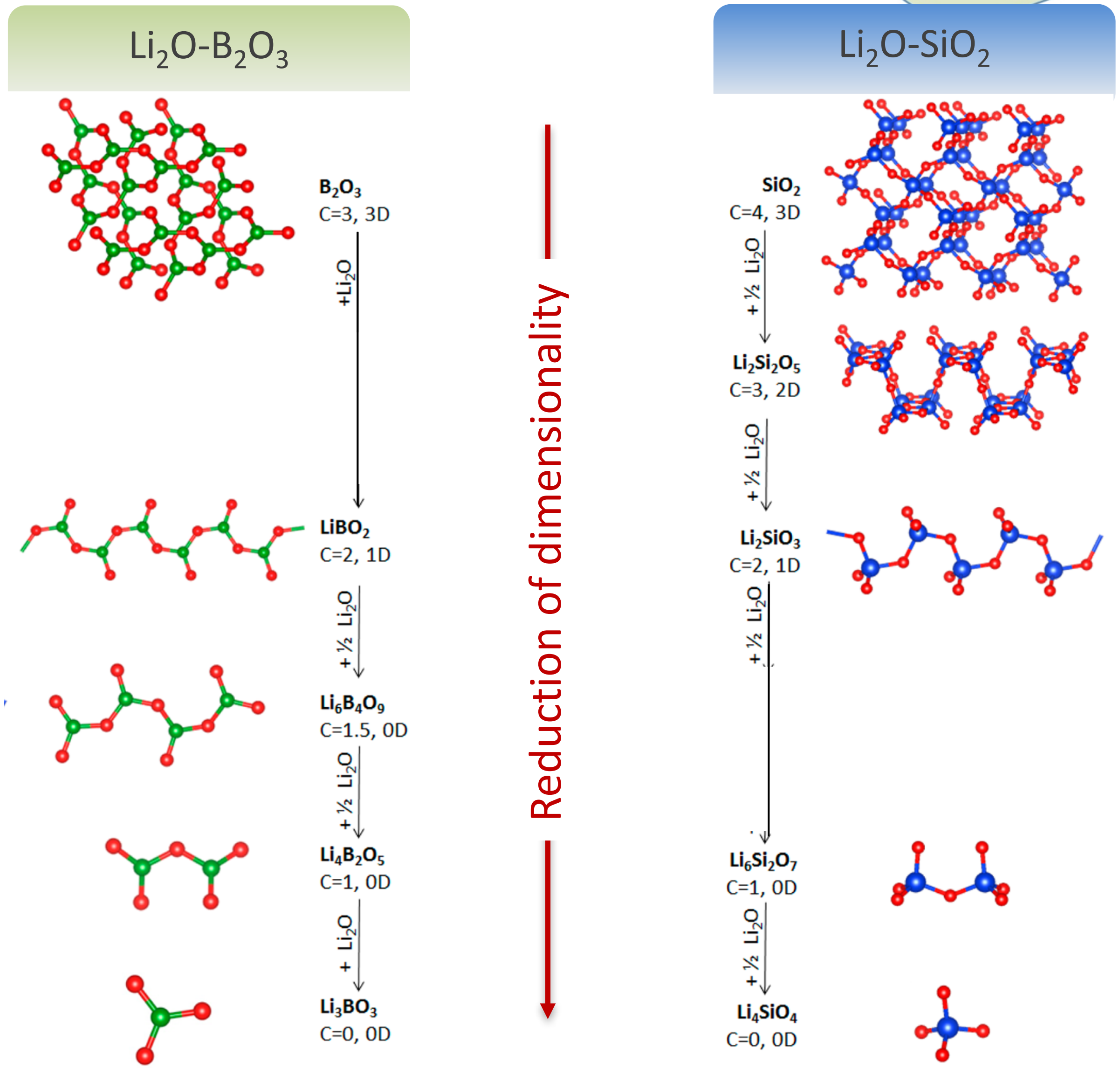
Li_2O-B_2O_3 SYSTEM





→ *Presence of complex structures called superstructural units*

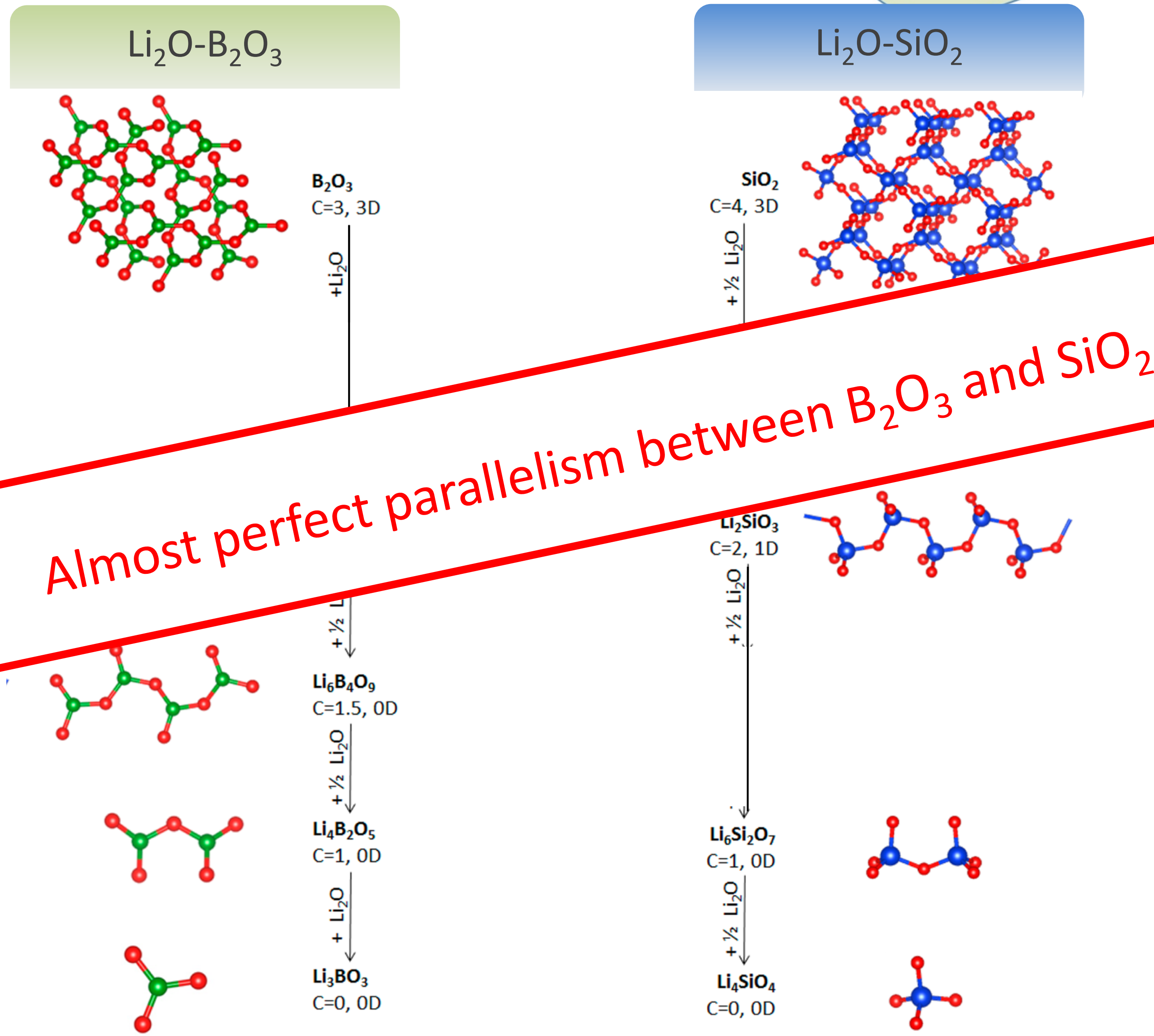
DEPOLYMERIZATION MECHANISMS



Rousse et al. Inorg. Chem. 2014

Tulsky et al. Chem. Mater. 2001

DEPOLYMERIZATION MECHANISMS



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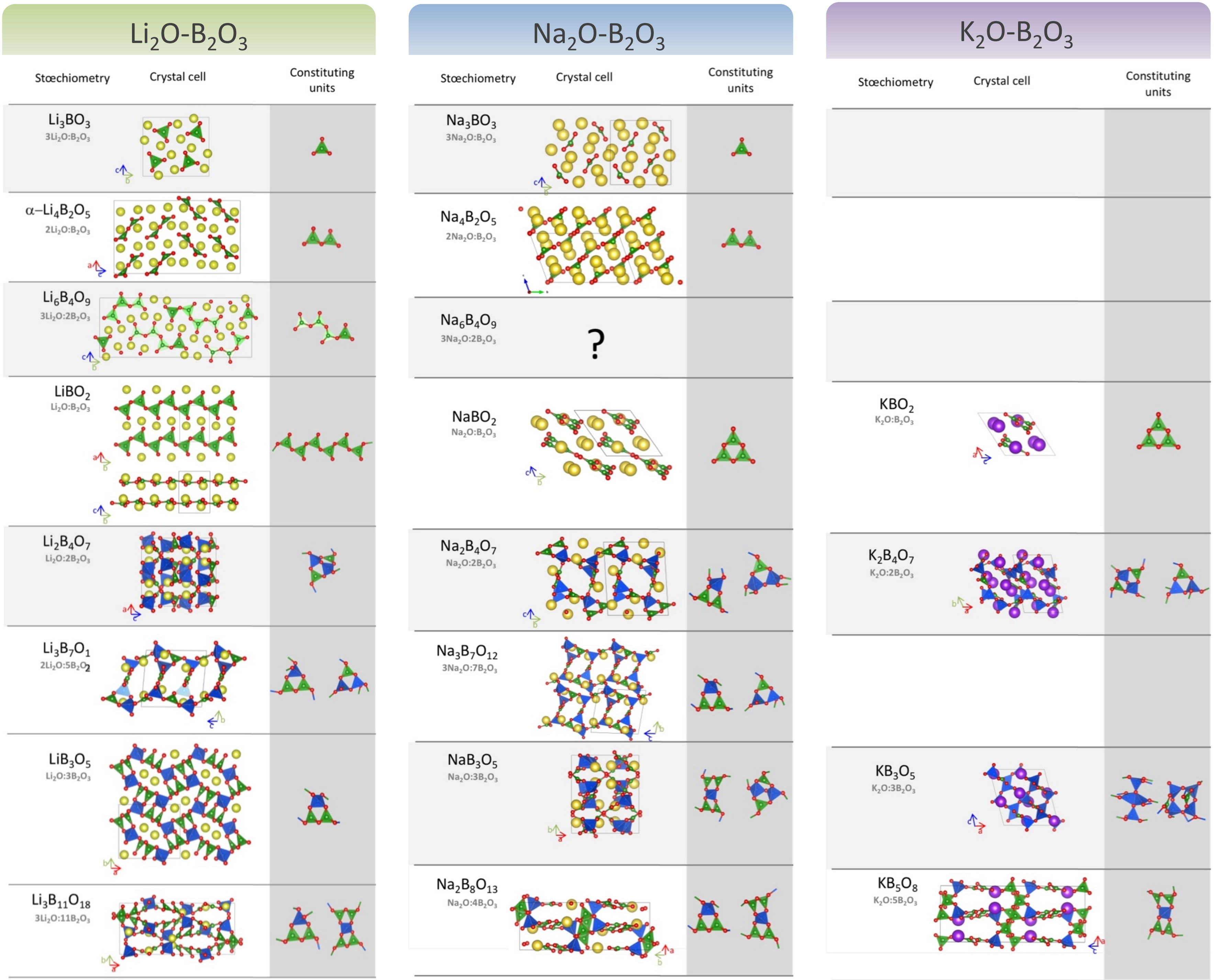
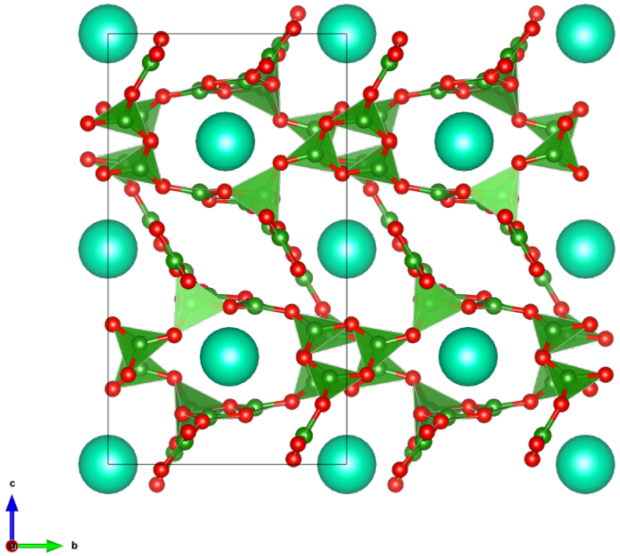


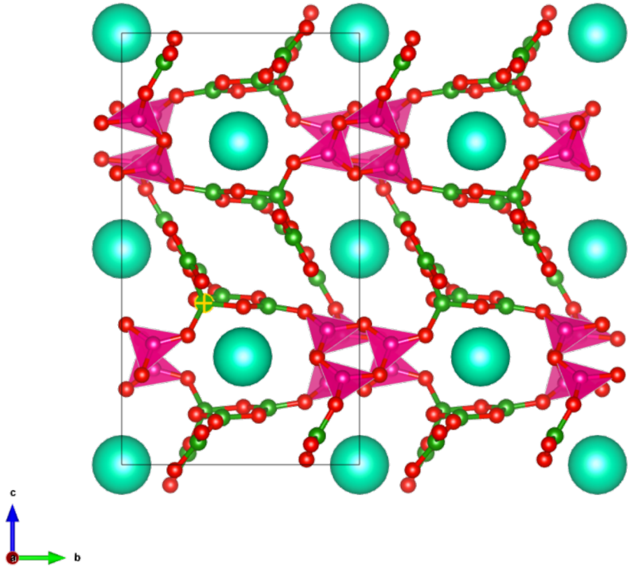
Li2O-B2O3
Stœchiometry
Crystal cell
Constituting units
Li3BO3
3Li2O:B2O3
α–Li4B2O5
2Li2O:B2O3
Li6B4O9
3Li2O:2B2O3
LiBO2
Li2O:B2O3
Li2B4O7
Li2O:2B2O3
Li3B7O1
2Li2O:5B2O2
LiB3O5
Li2O:3B2O3
Li3B11O18
3Li2O:11B2O3
Na2O-B2O3
Stœchiometry
Crystal cell
Constituting units
Na3BO3
3Na2O:B2O3
Na4B2O5
2Na2O:B2O3
Na6B4O9
3Na2O:2B2O3
?
NaBO2
Na2O:B2O3
Na2B4O7
Na2O:2B2O3
Na3B7O12
3Na2O:7B2O3
NaB3O5
Na2O:3B2O3
Na2B8O13
Na2O:4B2O3
K2O-B2O3
Stœchiometry
Crystal cell
Constituting units
KBO2
K2O:B2O3
K2B4O7
K2O:2B2O3
KB3O5
K2O:3B2O3
KB5O8
K2O:5B2O3

CAESIUM ENEABORATE CASE



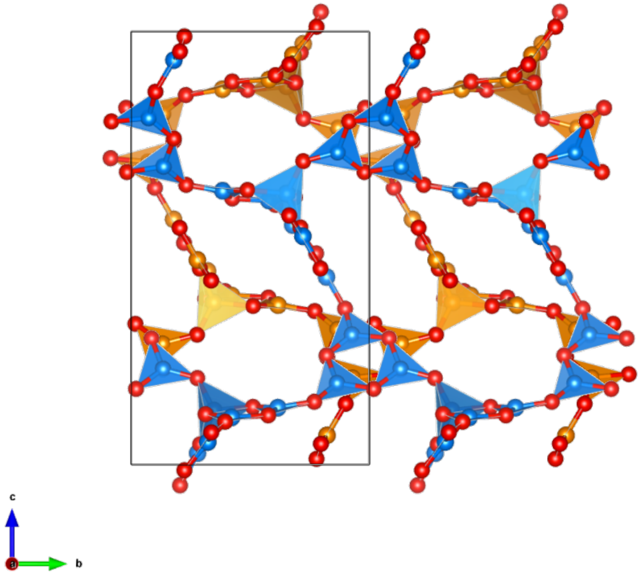
- 90% BO_3 units

CAESIUM ENEABORATE CASE



- 90% BO_3 units
- Unique crystal containing **boroxol rings**
- 30% of BO_3 units involved in boroxol rings

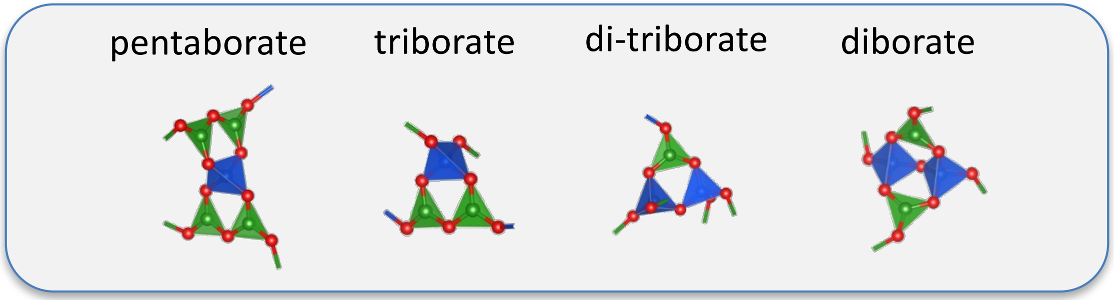
CAESIUM ENEABORATE CASE



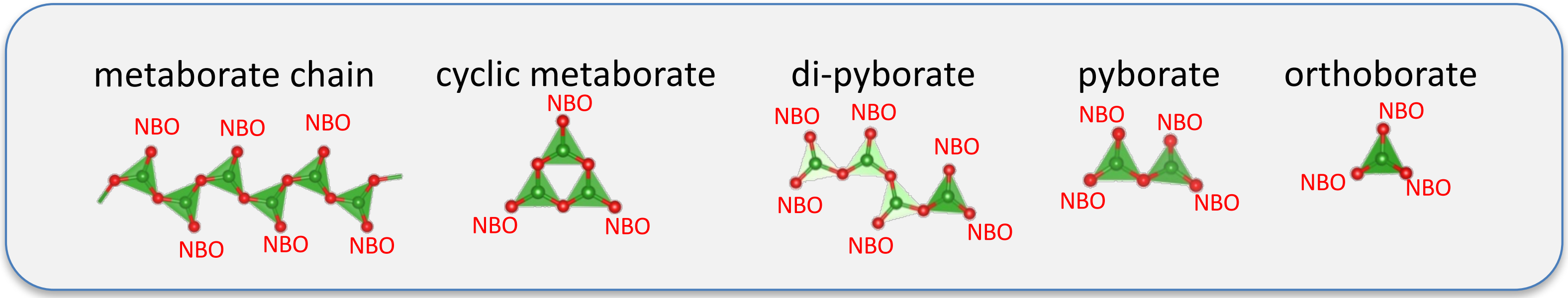
- 90% BO_3 units
- Unique crystal containing **boroxol rings**
- 30% of BO_3 units involved in boroxol rings
- 2 independent sub-networks

ZOOLOGY OF THE SUPERSTRUCTURAL UNITS

- Examples of units containing [3]B and [4]B



- Examples of units containing only [3]B



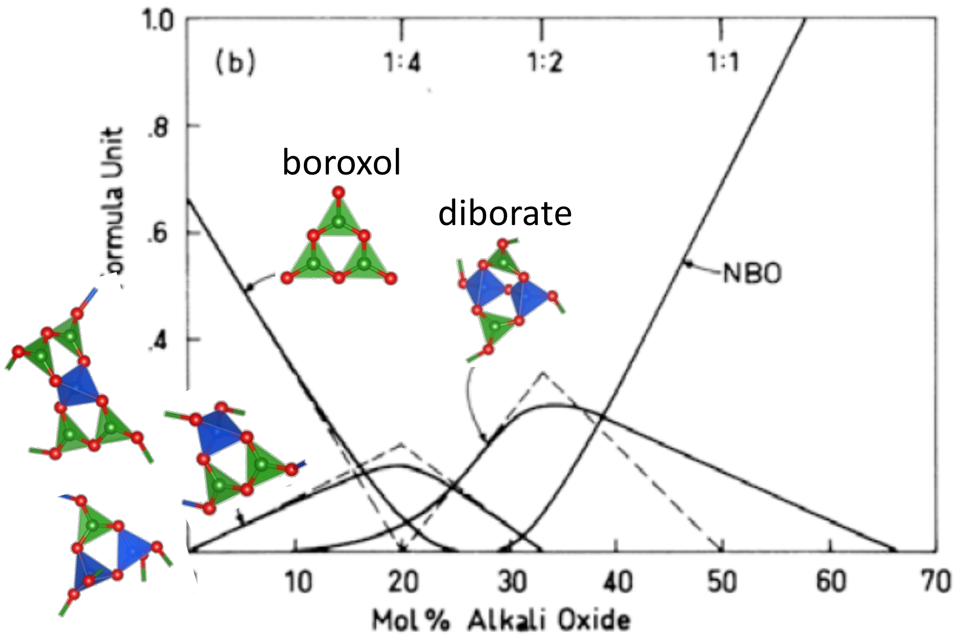
→ *Existence of an intermediate range order in glasses ???*

Borate glasses – Structure

NMR	^{11}B (NA: 80%) is the most sensitive **+ +** ^{17}O (NA: 0.038%) is the only NMR active nucleus ⟶ Isotopic enrichment mandatory **+ -**
Raman **IR**	Well suited **+ +**
ND **neutron**	^{11}B is highly absorbing ⟶ Isotopic enrichment mandatory **+ -**
XAS **X-rays**	Low-Z elements ⟶ K-edges are surface sensitive – high-vacuum mandatory **+ -**

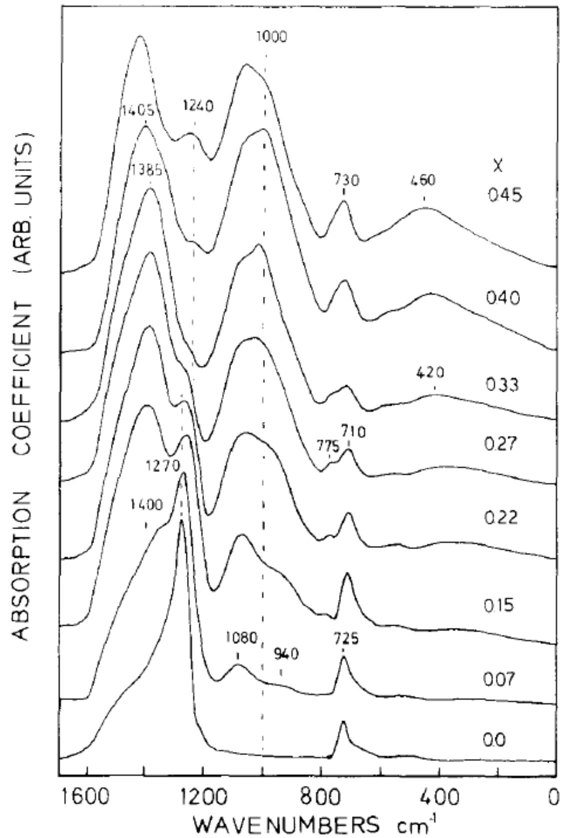
KROGH-MOE – GRISCOM MODEL

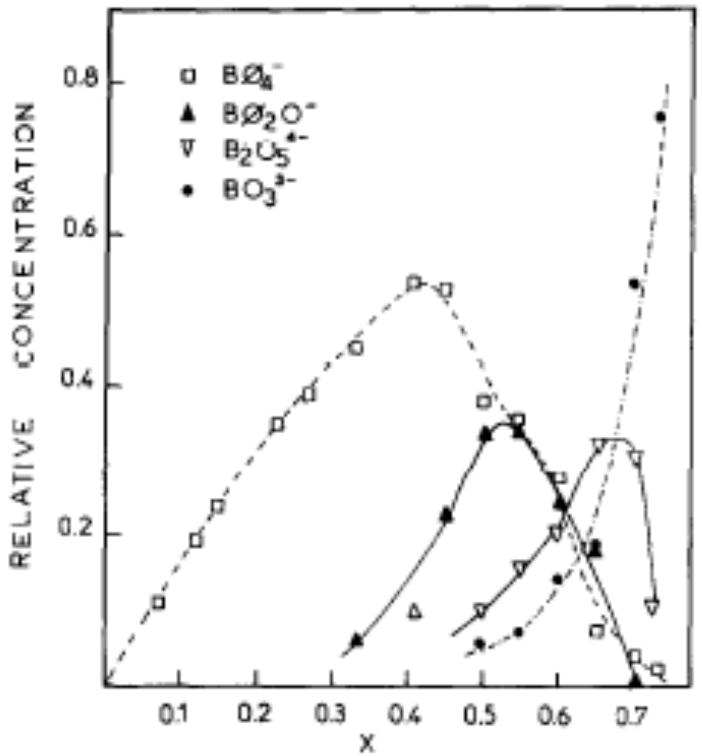
- Krogh-Moe in 1962 predicted the distribution of superstructural units in sodium borate glasses as a function of Na_2O content.



Krogh-Moe PCG 1962

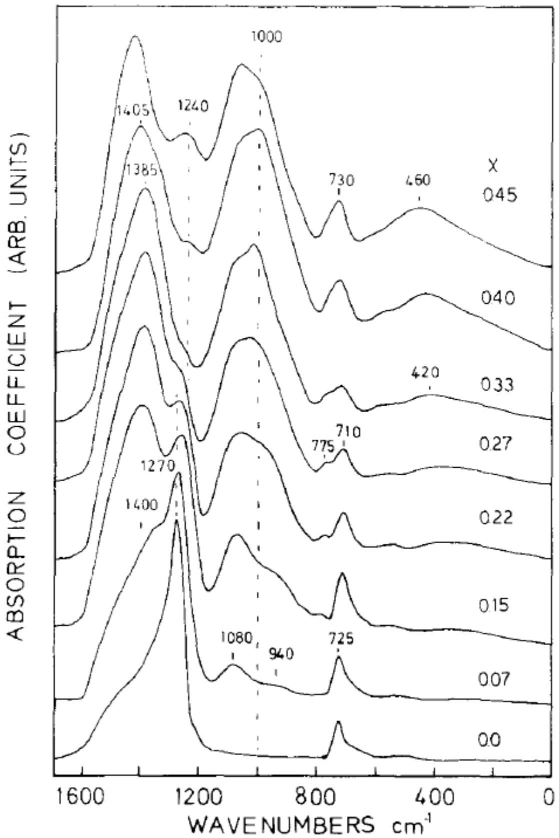
SUPERSTRUCTURAL UNITS BY IR AND RAMAN SPECTROSCOPIES

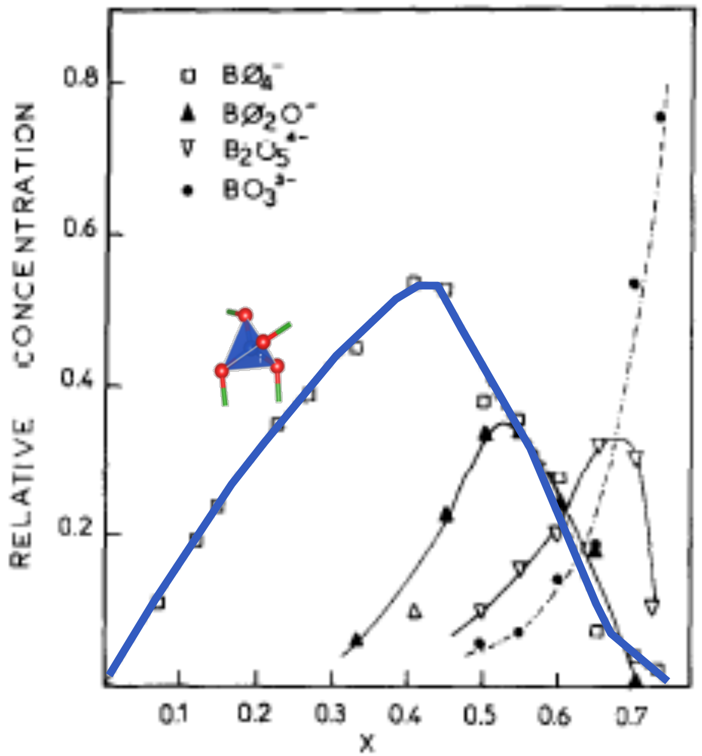




Kamitsos et al. J. Mol. Struct. 347, 1-16 (1991) / Kamitsos et al. JNCS 126, 52-67 (1990)

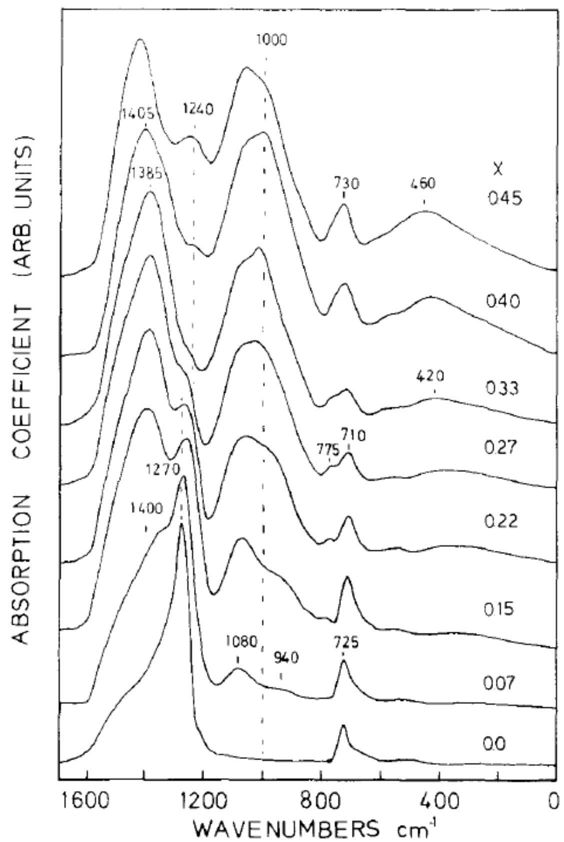
Superstructural units by IR and Raman Spectroscopies

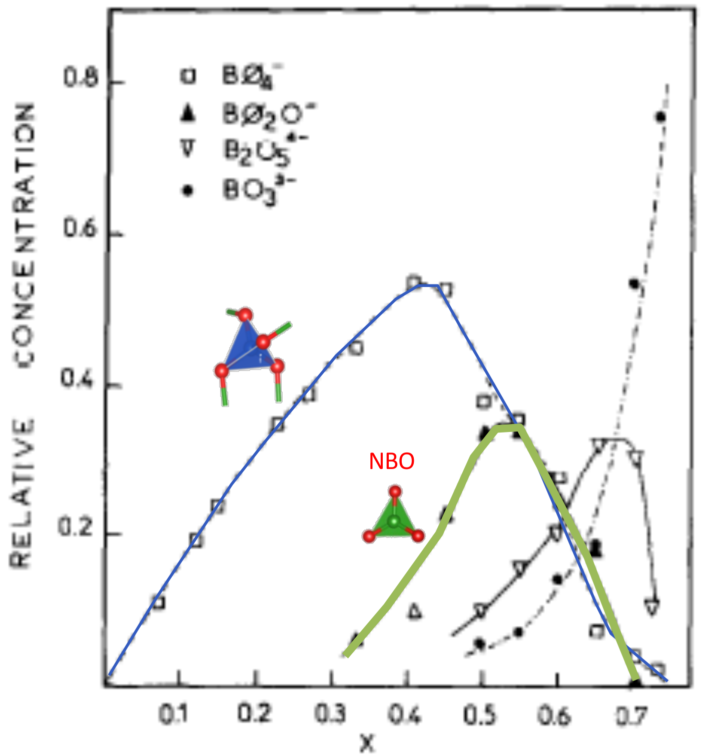




Kamitsos et al. J. Mol. Struct. 347, 1-16 (1991) / Kamitsos et al. JNCS 126, 52-67 (1990)

SUPERSTRUCTURAL UNITS BY IR AND RAMAN SPECTROSCOPIES





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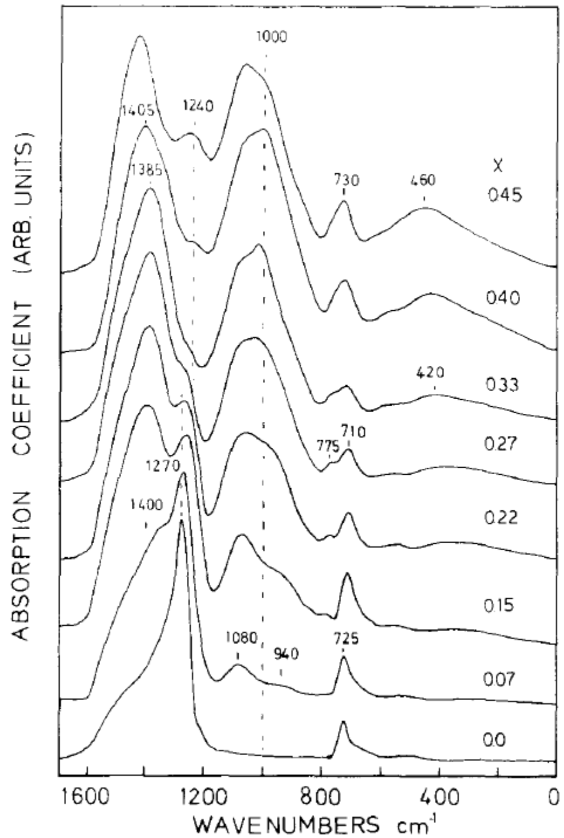
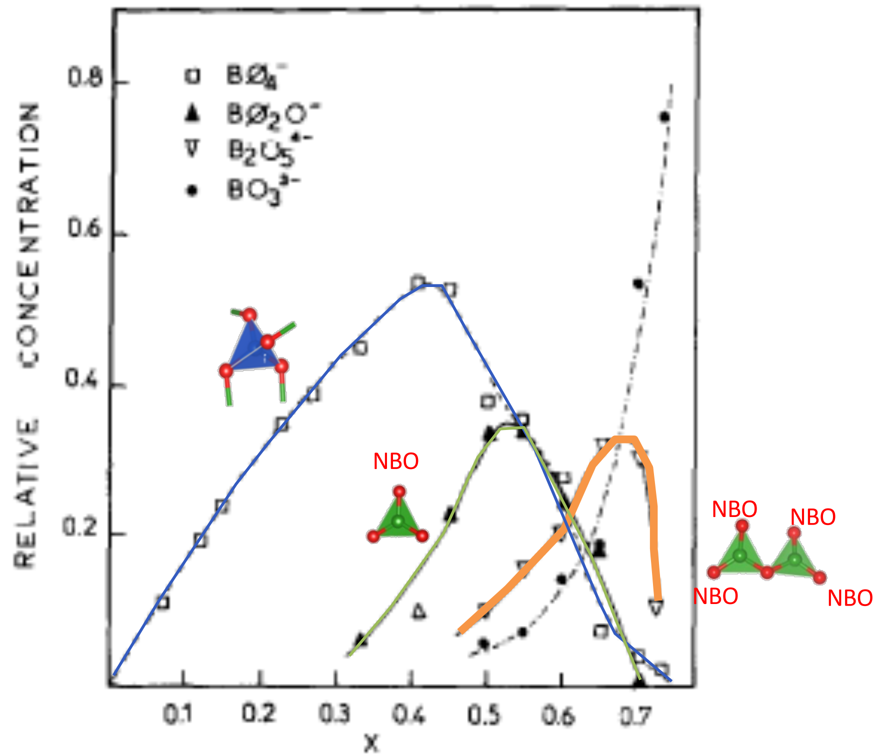
SUPERSTRUCTURAL UNITS BY IR AND RAMAN SPECTROSCOPIES





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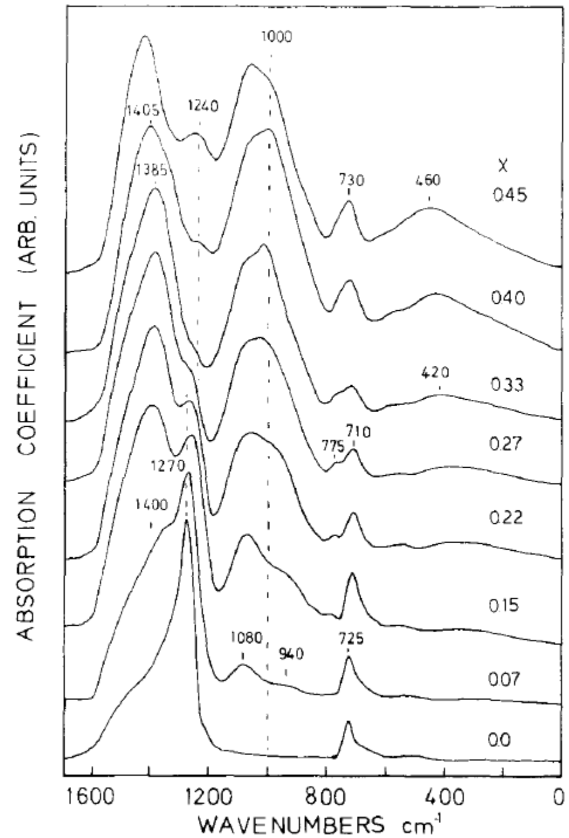
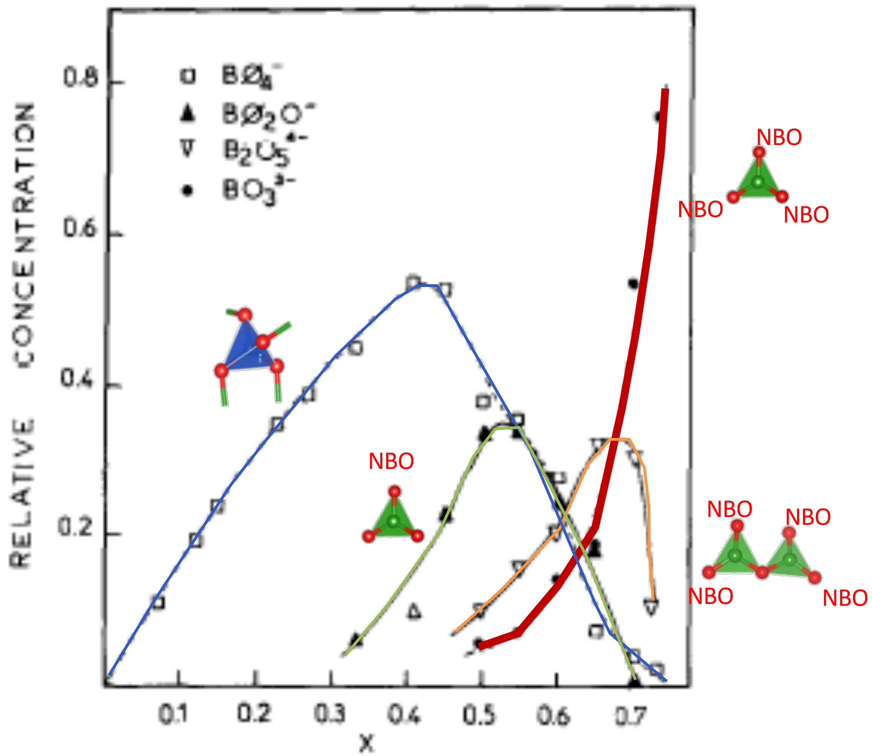
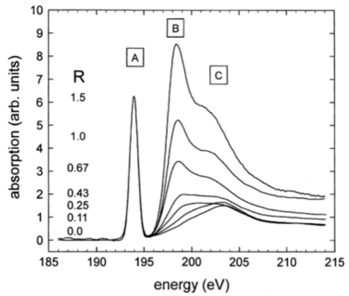
SUPERSTRUCTURAL UNITS BY IR AND RAMAN SPECTROSCOPIES





Kamitsos et al. J. Mol. Struct. 347, 1-16 (1991) / Kamitsos et al. JNCS 126, 52-67 (1990)

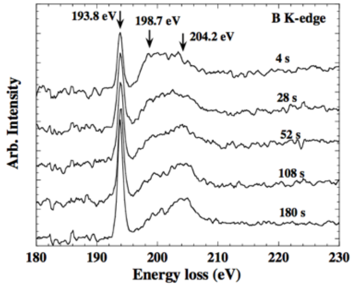
PROBING LOCAL ORDER AND ELECTRONIC STRUCTURE



X-ray absorption spectroscopy (XAS)

⇒High vacuum – Surface sensitive - High resolution (<0.2 eV)

⇒No complex sample environments

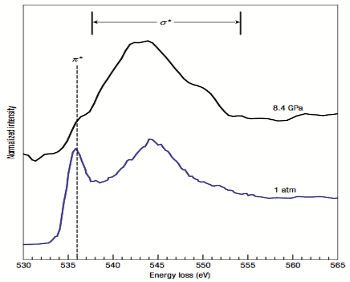


Energy Electron Loss Spectroscopy (EELS)

⇒Vacuum – Beam damage – Low resolution (~ 0.7 eV)

⇒Access to edges at very low energies (Li), spatial resolution

⇒No complex sample environments



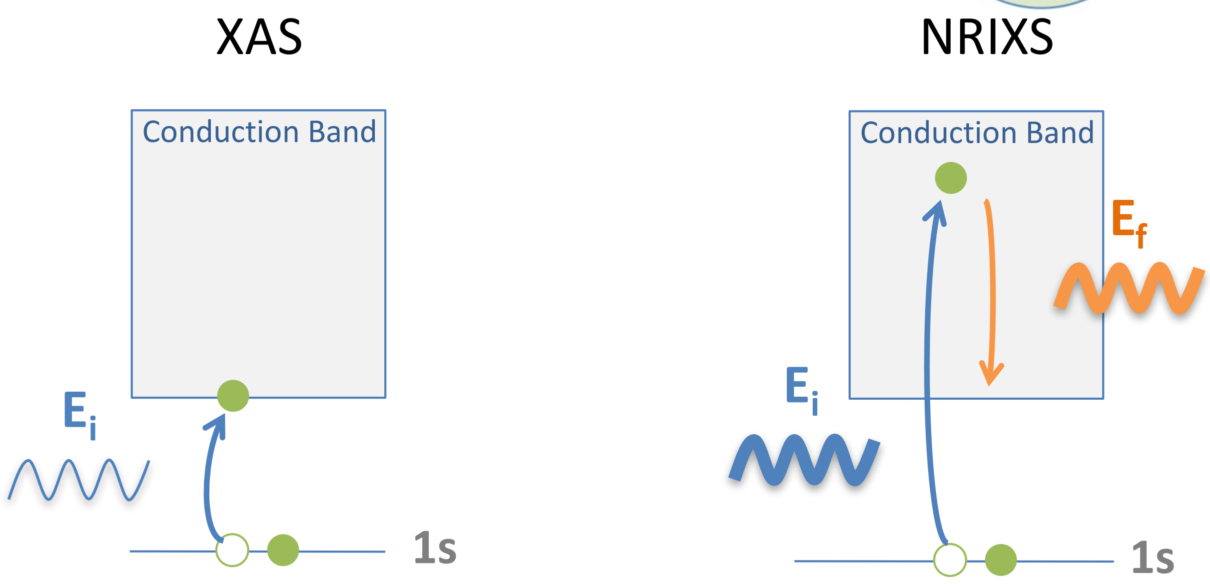
Non-resonant Inelastic X-ray scattering (NRIXS)

⇒Low resolution (~ 0.7 eV) – Long experiments

⇒Access to edges at very low energies (Li ⇒ Ne)

⇒Various complex sample environments (high-pressure, high-temperature…)

NRIXS: A SUBSTITUTE FOR SOFT X-RAY XAS

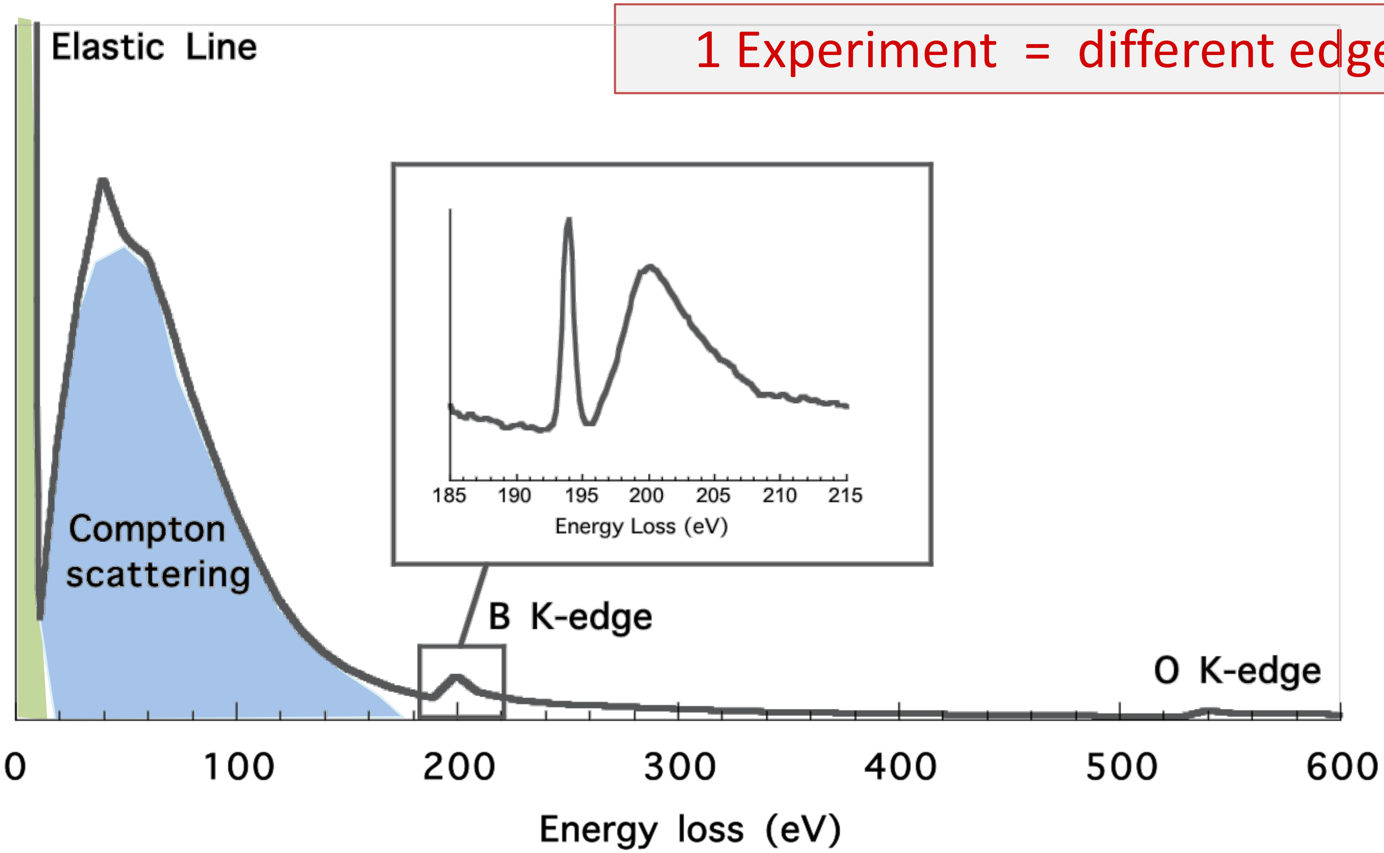


For low-Z elements:

XAS	NRIXS
soft x-rays	hard x-rays
surface sensitive	bulk sensitive
vacuum condition	**atmospheric condition**
	complex sample environments

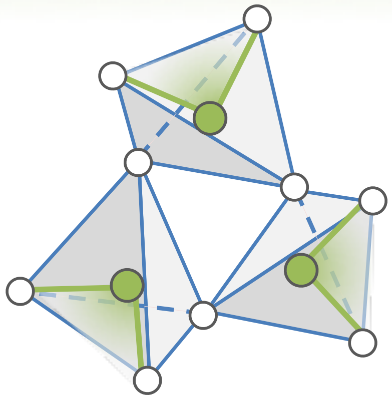
NRIXS: A SUBSTITUTE FOR SOFT X-RAY XAS

1 Experiment = different edges !



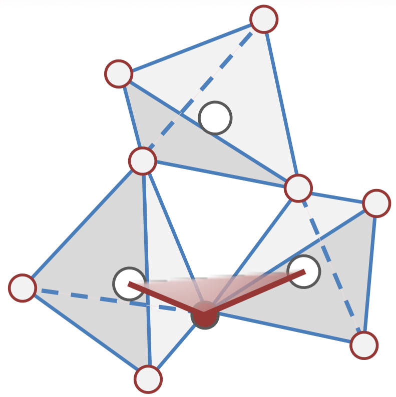
STRUCTURE OF OXIDE GLASSES USING X-RAYS

VIEW THROUGH THE NETWORK FORMER CATIONS



B K-edge

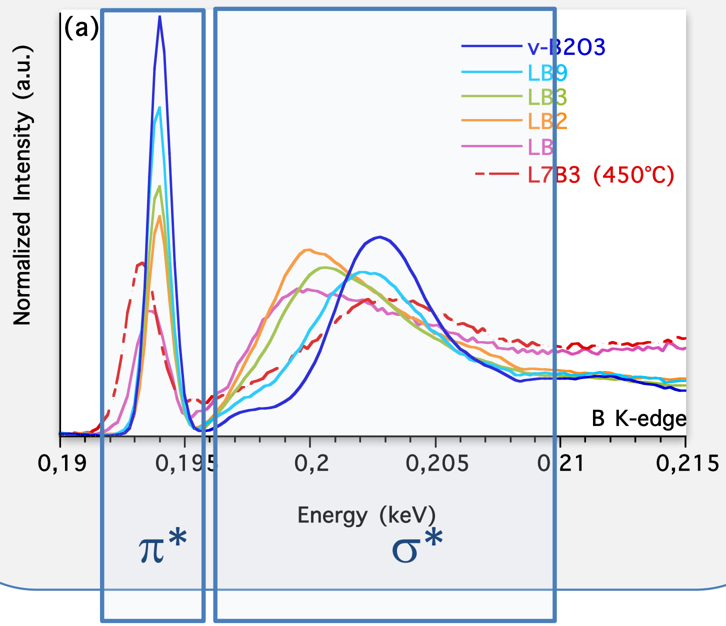
VIEW THROUGH THE LIGANDS



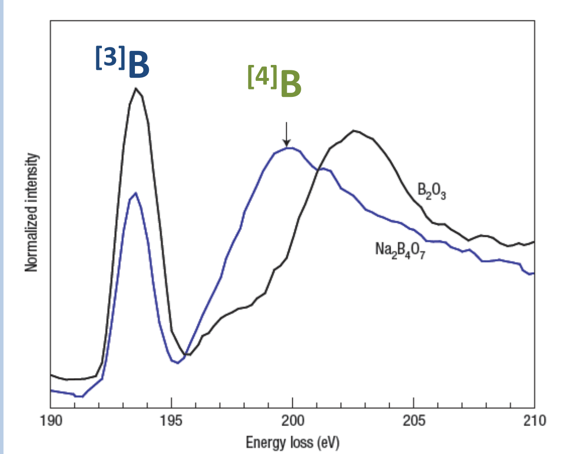
O K-edge

B K-EDGE IN LITHIUM BORATE GLASSES

B K-edge (T = 21°C)

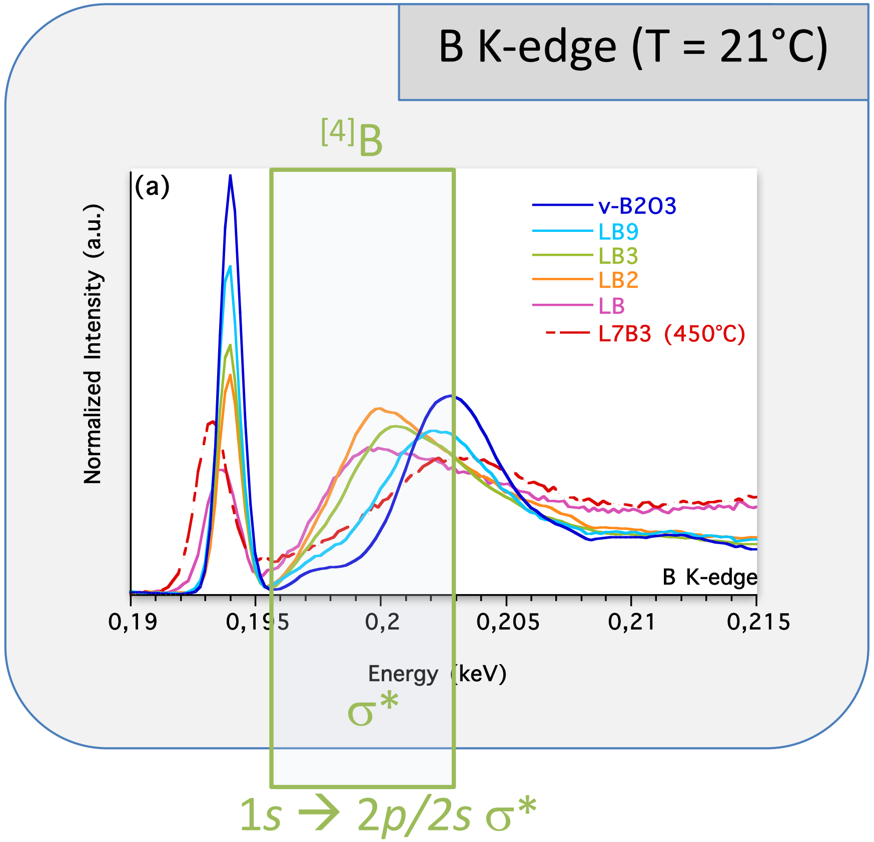


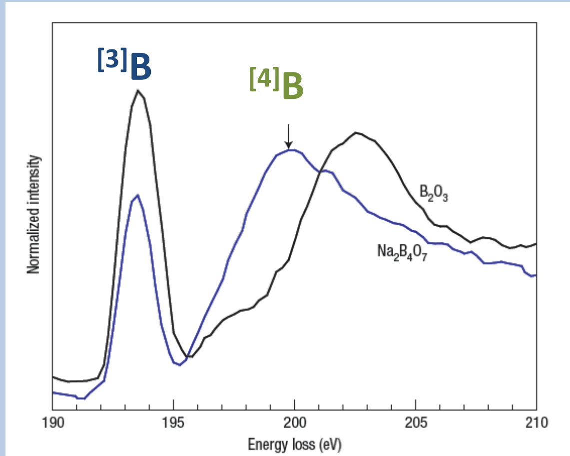
$1s \rightarrow 2p_z$ $1s \rightarrow$ B-O σ^*



Lee *et al.*, Nature materials (2005) 4, 851-854.

B K-EDGE IN LITHIUM BORATE GLASSES



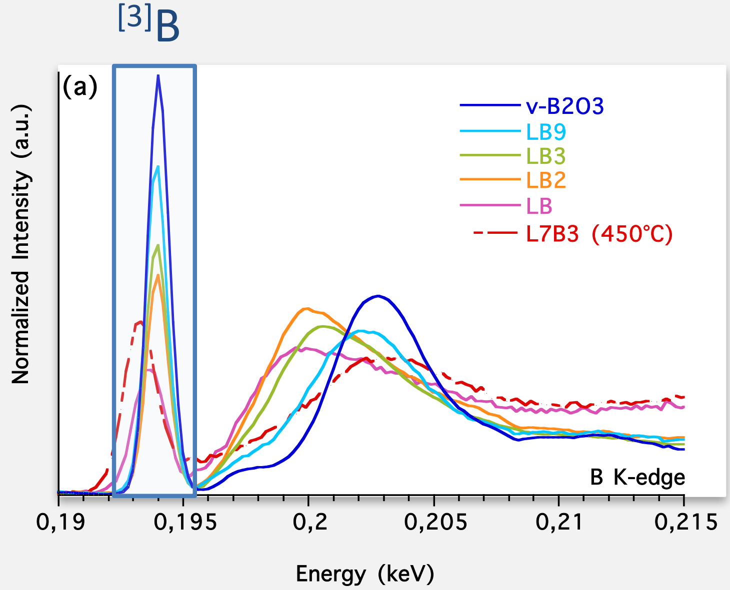


Lee *et al.*, Nature materials (2005) 4, 851-854.

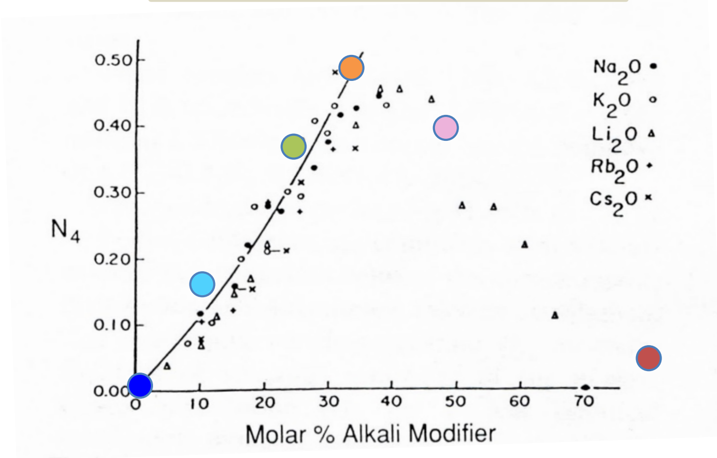
Modifications of the B K-edge due to the BO_3 / BO_4 ratio

Effect of Li content on the $^{[3]}B/^{[4]}B$

B K-edge (T = 21°C)

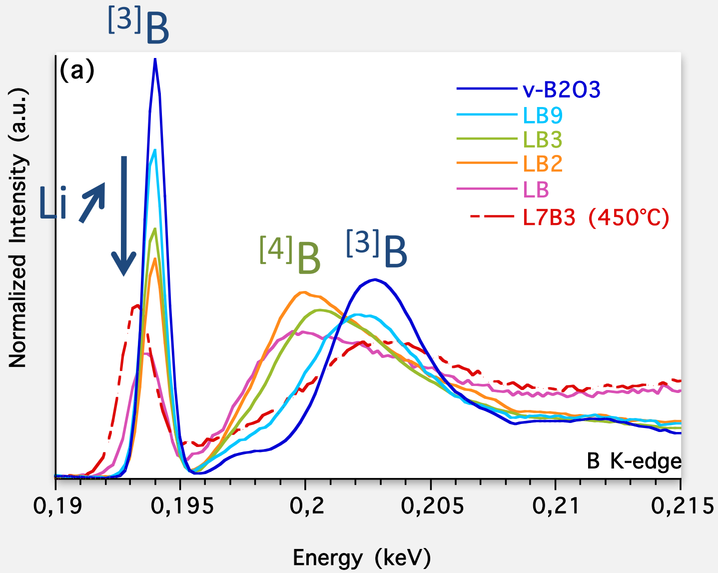


Zhong JNCS 1989, 111, 67.



WHAT CAN WE LEARN FROM THE O K-EDGE ?

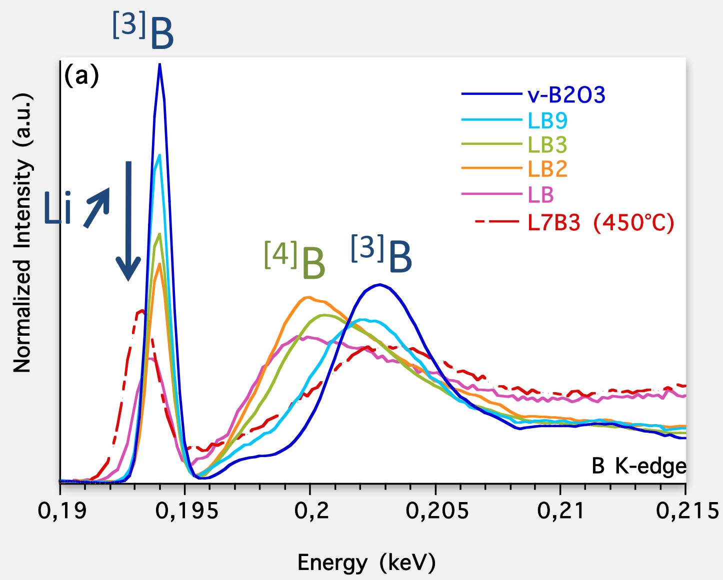
B K-edge (T = 21°C)



Coordination change for B

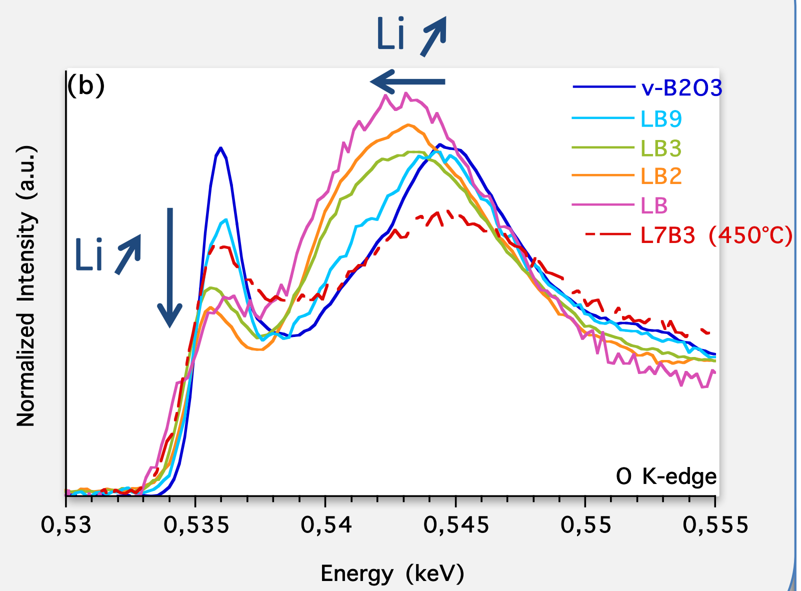
WHAT CAN WE LEARN FROM THE O K-EDGE ?

B K-edge (T = 21°C)



Coordination change for B

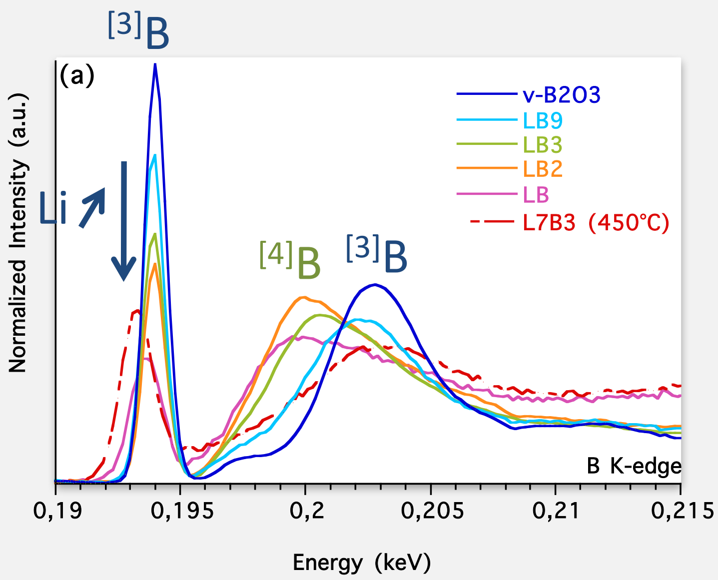
O K-edge (T = 21°C)



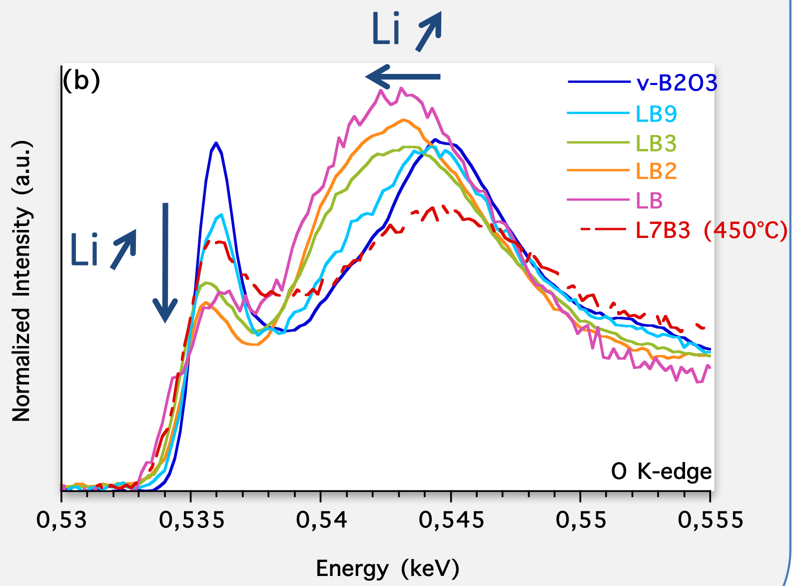
No coordination change for O

WHAT CAN WE LEARN FROM THE O K-EDGE ?

B K-edge (T = 21°C)

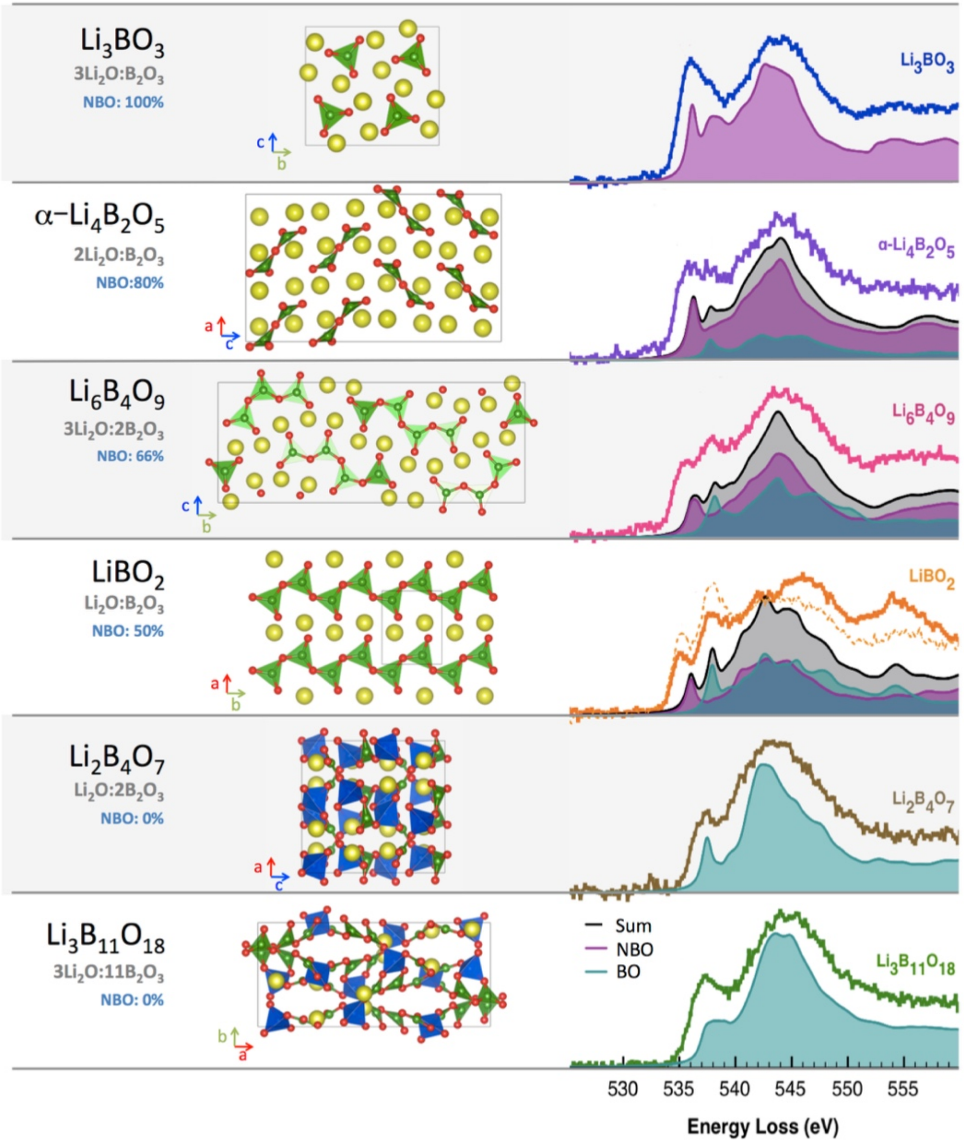


O K-edge (T = 21°C)



→ We need crystalline samples in order to better understand the O K-edge

O K-EDGE ON LI BORATE CRYSTALS



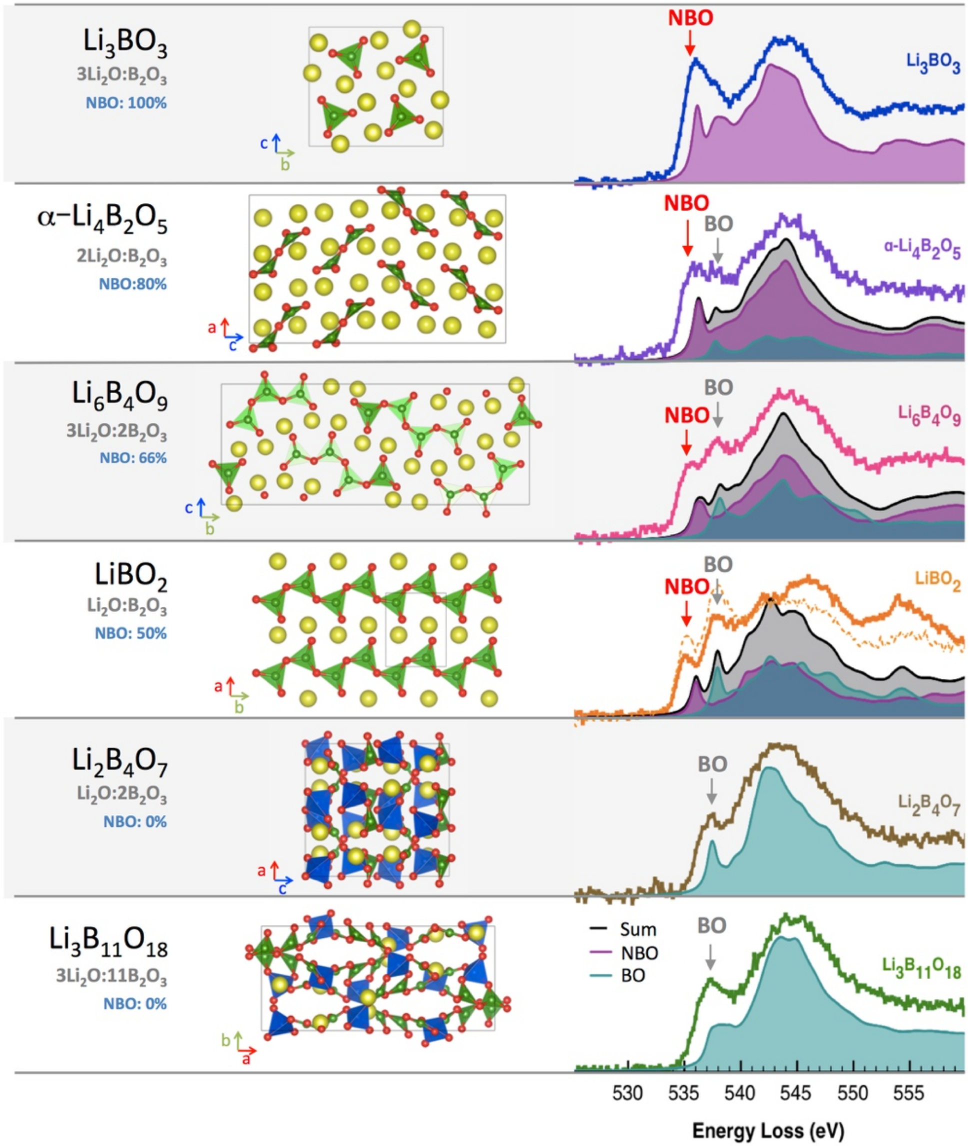
DFT Calculations

Contribution from NBOs

Contribution from BOs

Lelong, G. et al. J. Inorg. Chem. 2014, 53(20), 10903 .

O K-edge on Li borate crystals



DFT Calculations

- Contribution from NBOs
- Contribution from BOs

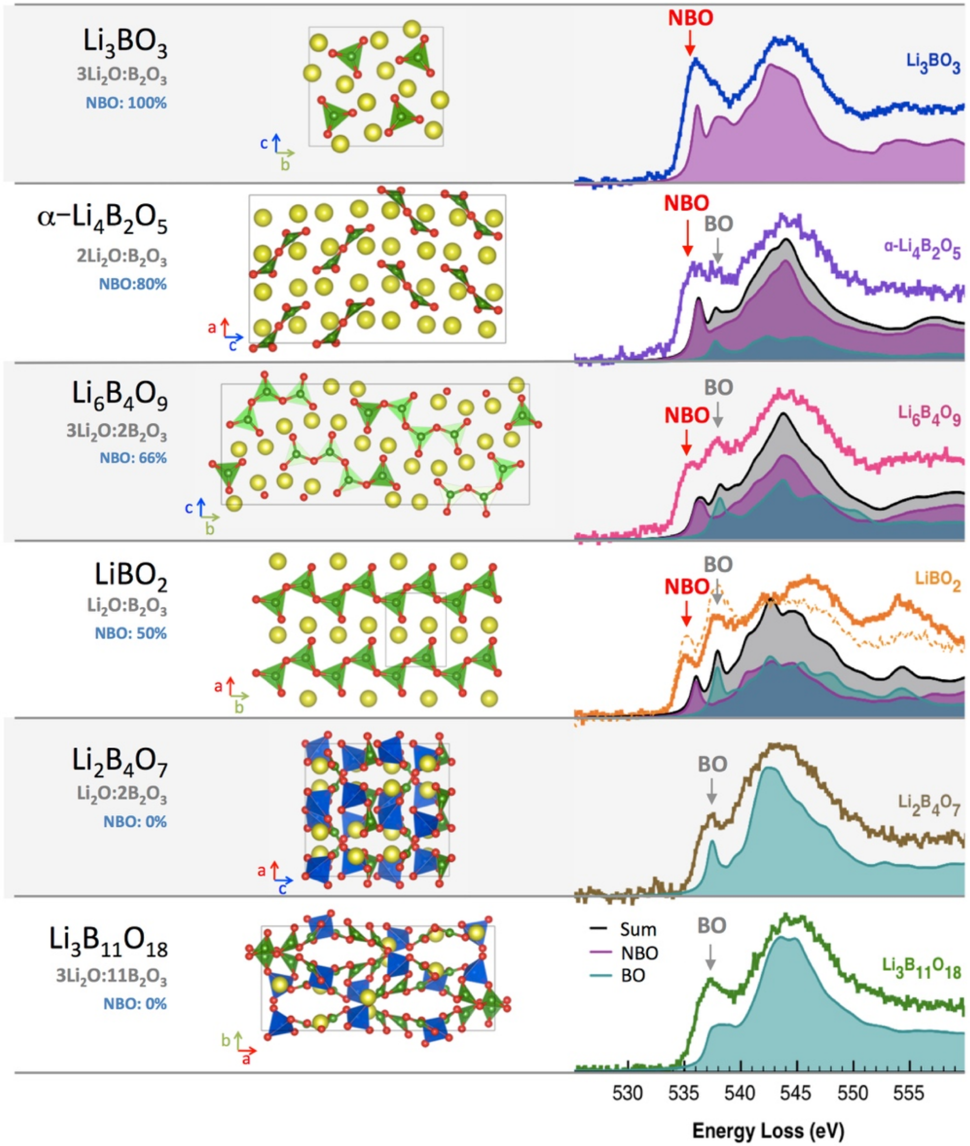
DETERMINATION OF A PROBE OF NBOs

↓

PROBE OF THE DEPOLYMERIZATION OF THE BORATE NETWORK

Lelong, G. et al. J. Inorg. Chem. 2014, 53(20), 10903 .

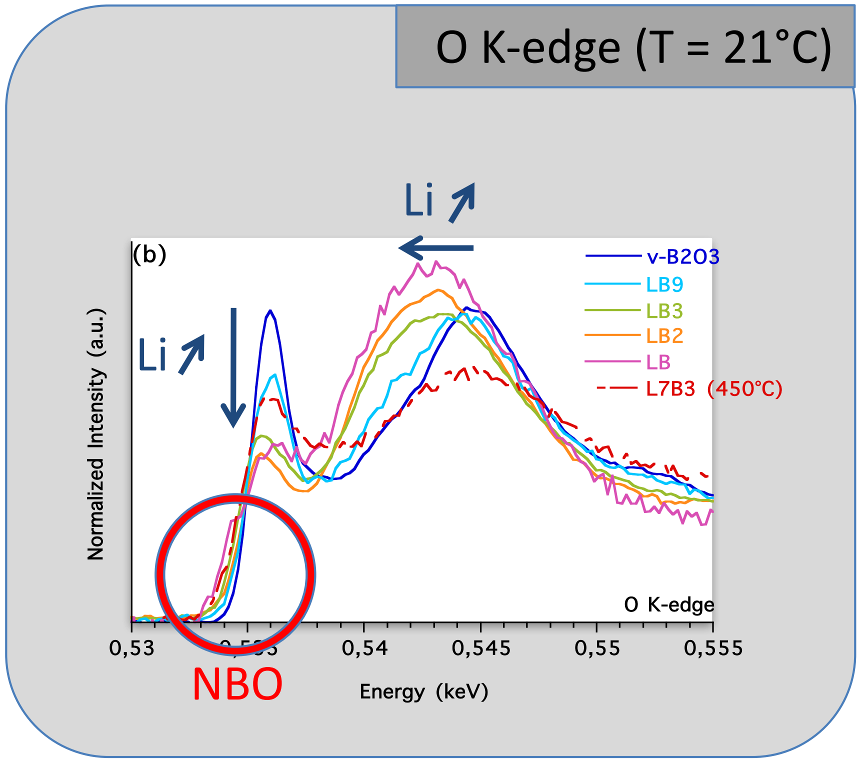
O K-edge on Li borate crystals



DFT Calculations

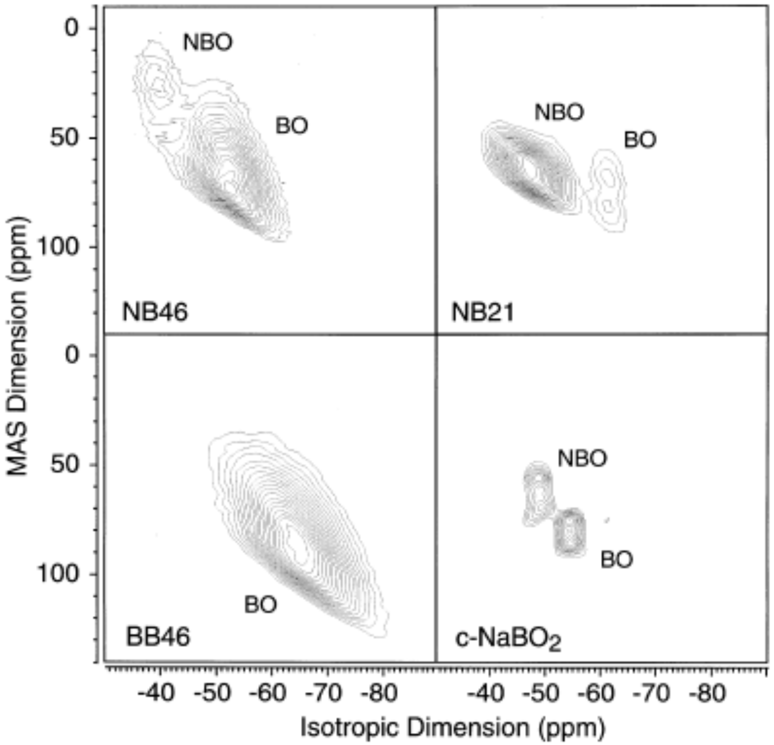
Contribution from NBOs

Contribution from BOs



Lelong et al. J. Inorg. Chem. 2014, 53(20), 10903 .

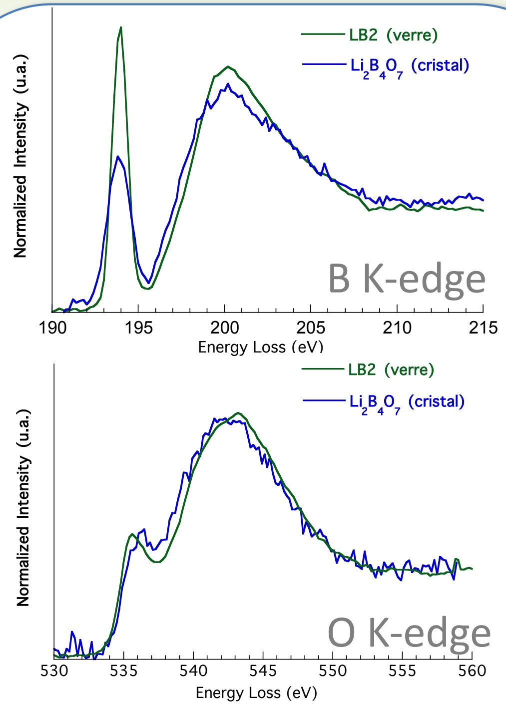
NBO BY ^{17}O NMR 3QMAS

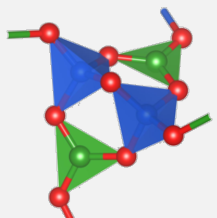


Stebbins et al. Solid State Magn. Res. 16, 9-19 (2000)

GLASSES VS CRYSTALS

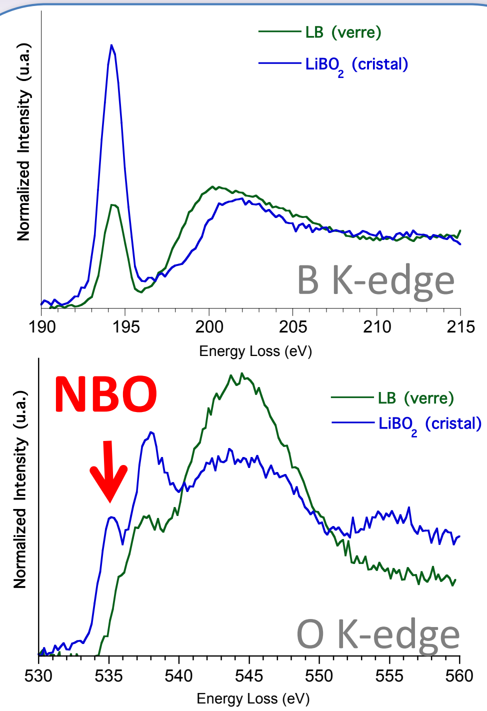
$Li_2O - 2B_2O_3$

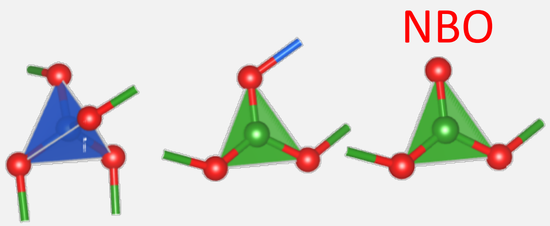




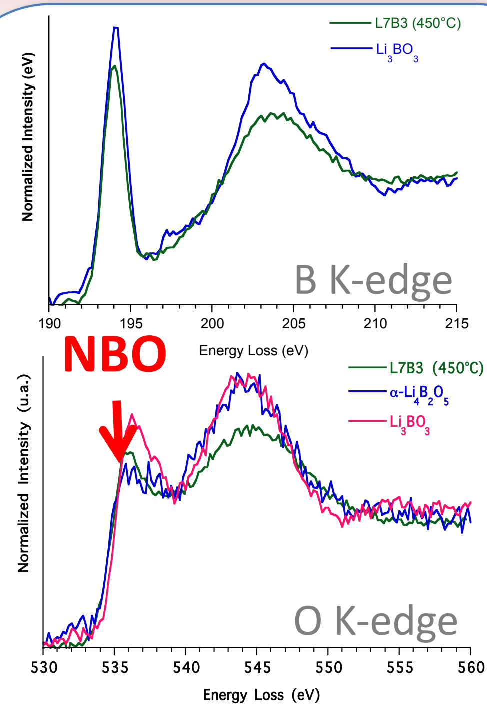
diborate groups

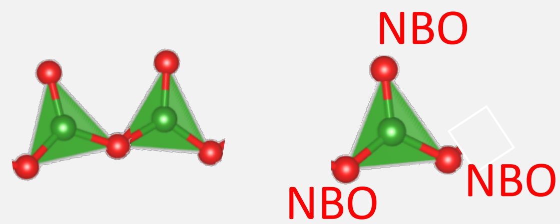
$Li_2O - B_2O_3$





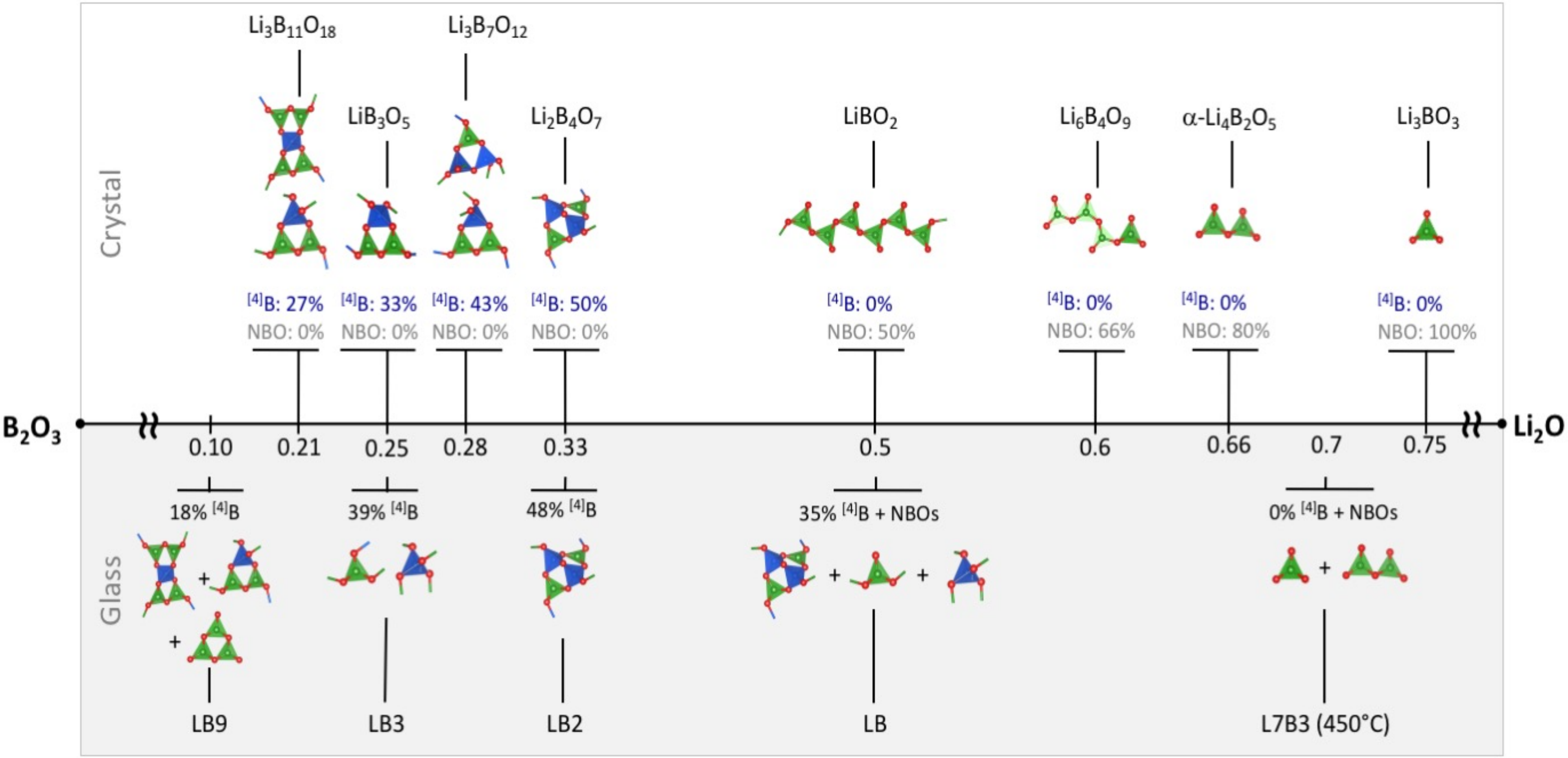
$3Li_2O - B_2O_3$





orthoborate

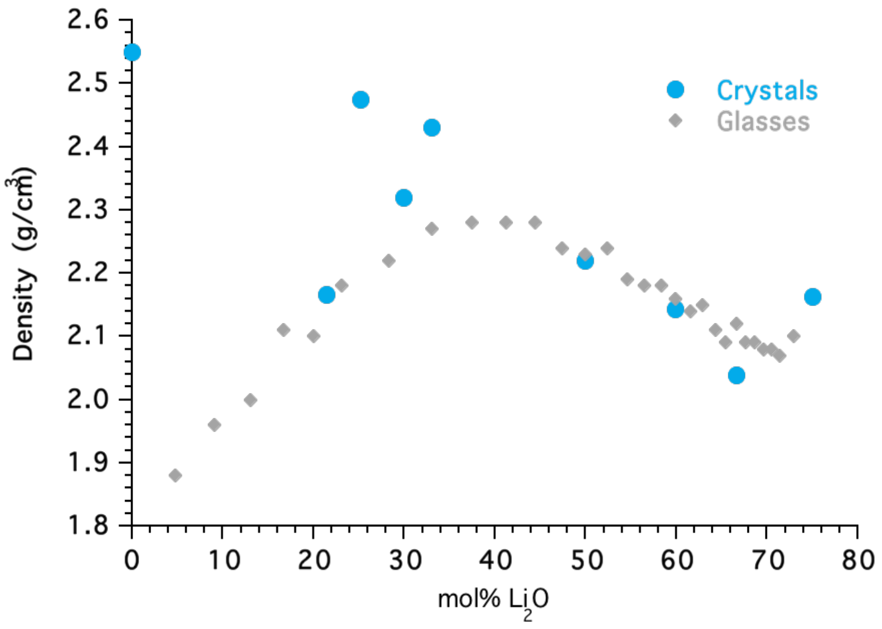
LITHIUM BORATES: GLASS VS. CRYSTAL



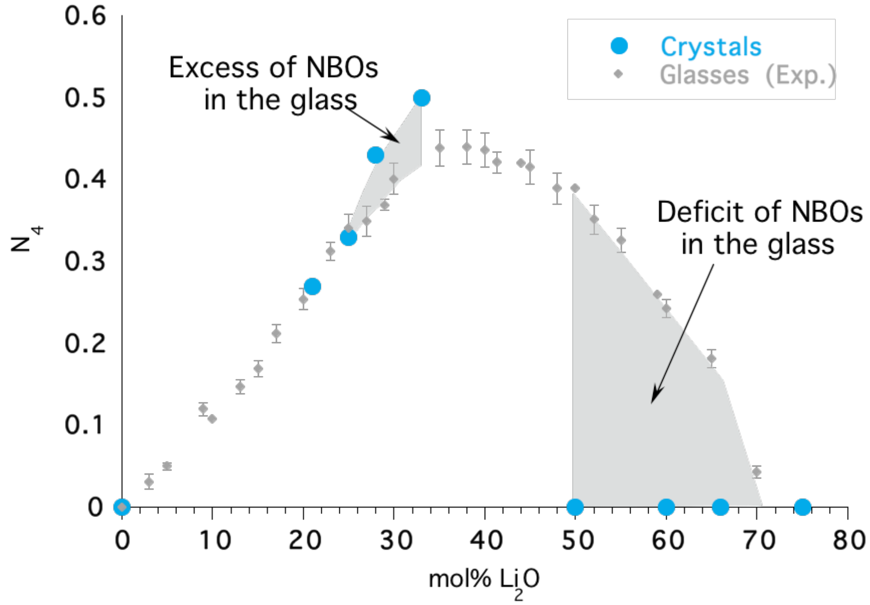
Lelong, G. et al. JNCS (2017) (submitted)

LITHIUM BORATES: GLASS VS. CRYSTAL

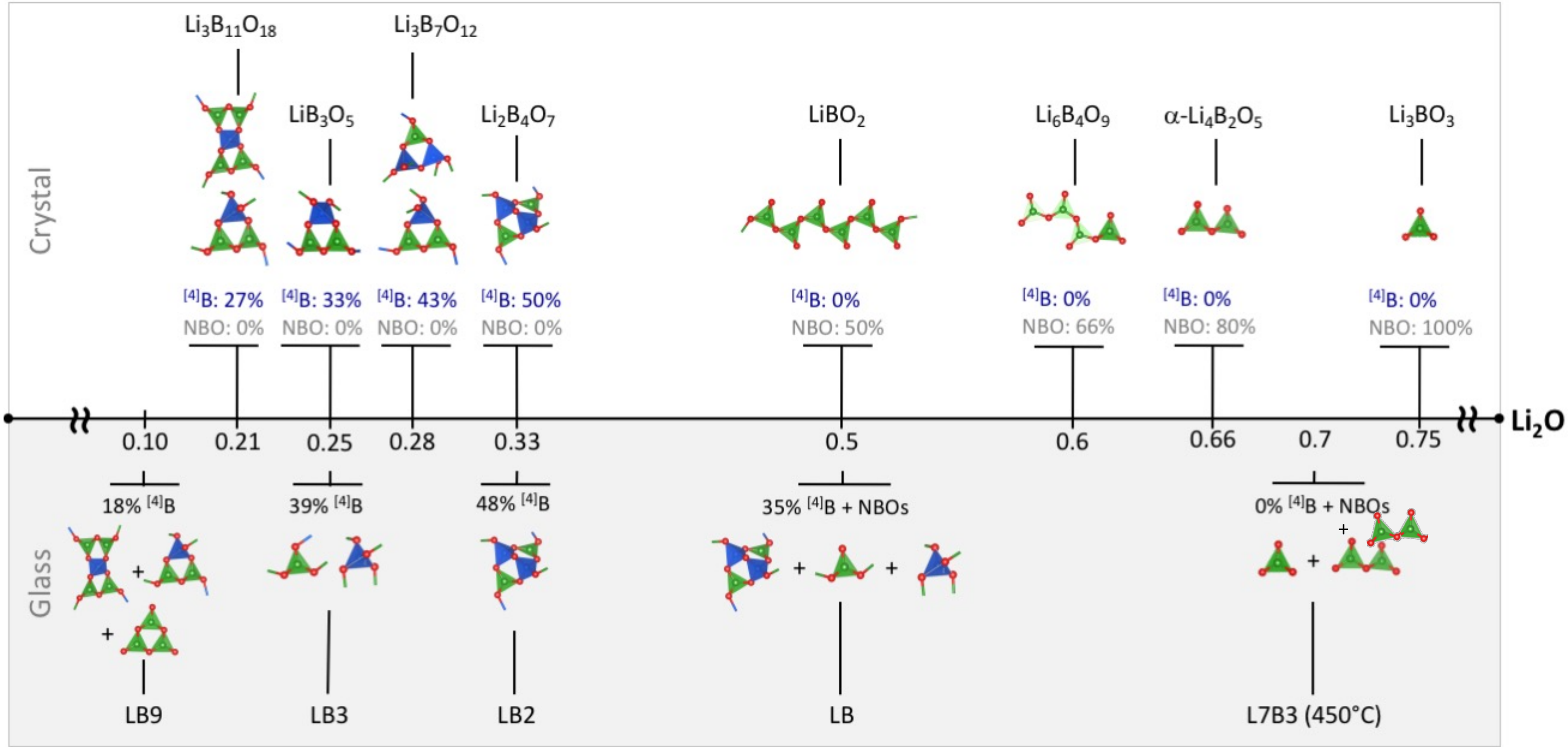
DENSITY



PROPORTION OF [4]B



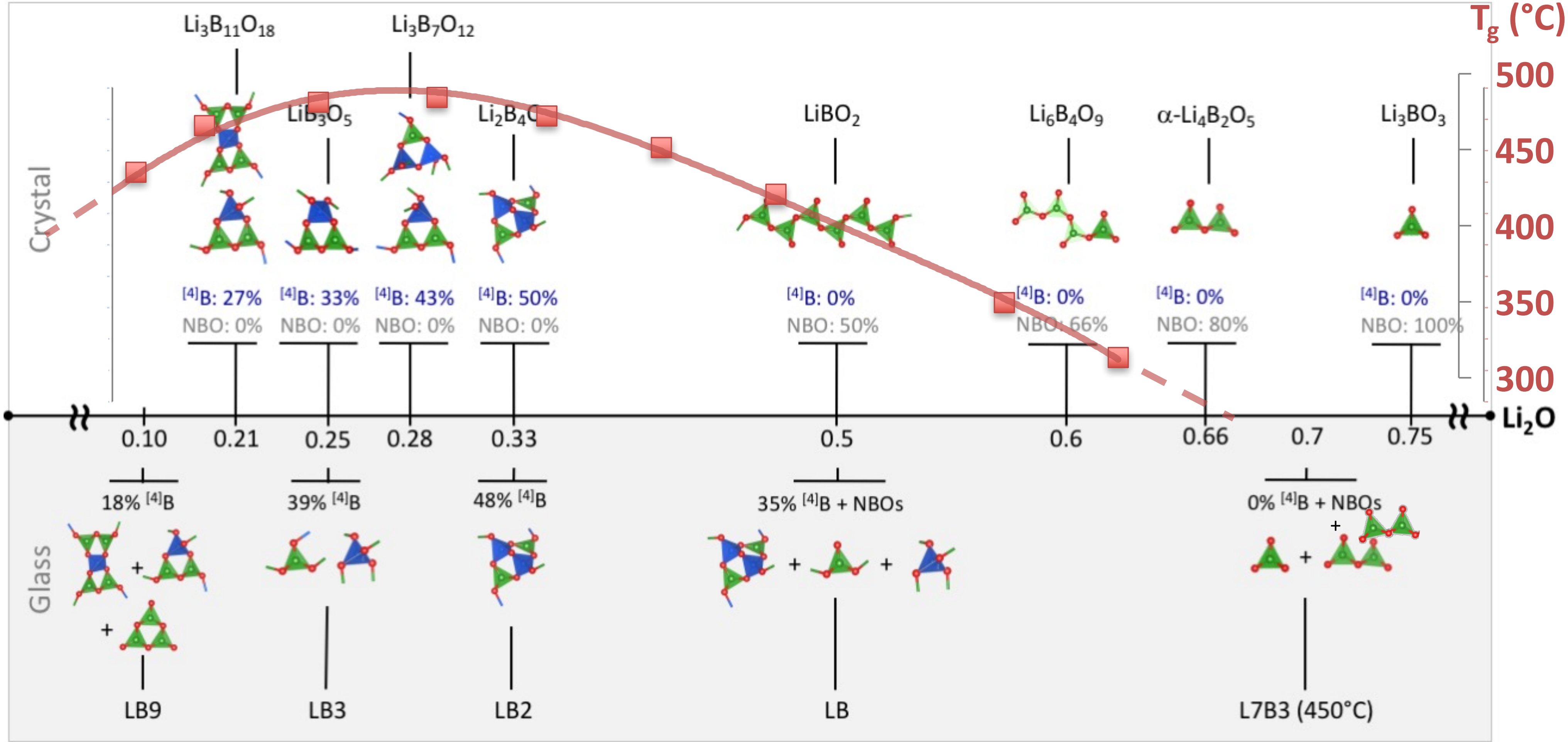
BORATE ANOMALIES …



Similarities glass ⟷cristal at the local scale

Discrepancies in the local structure of glass & cristal

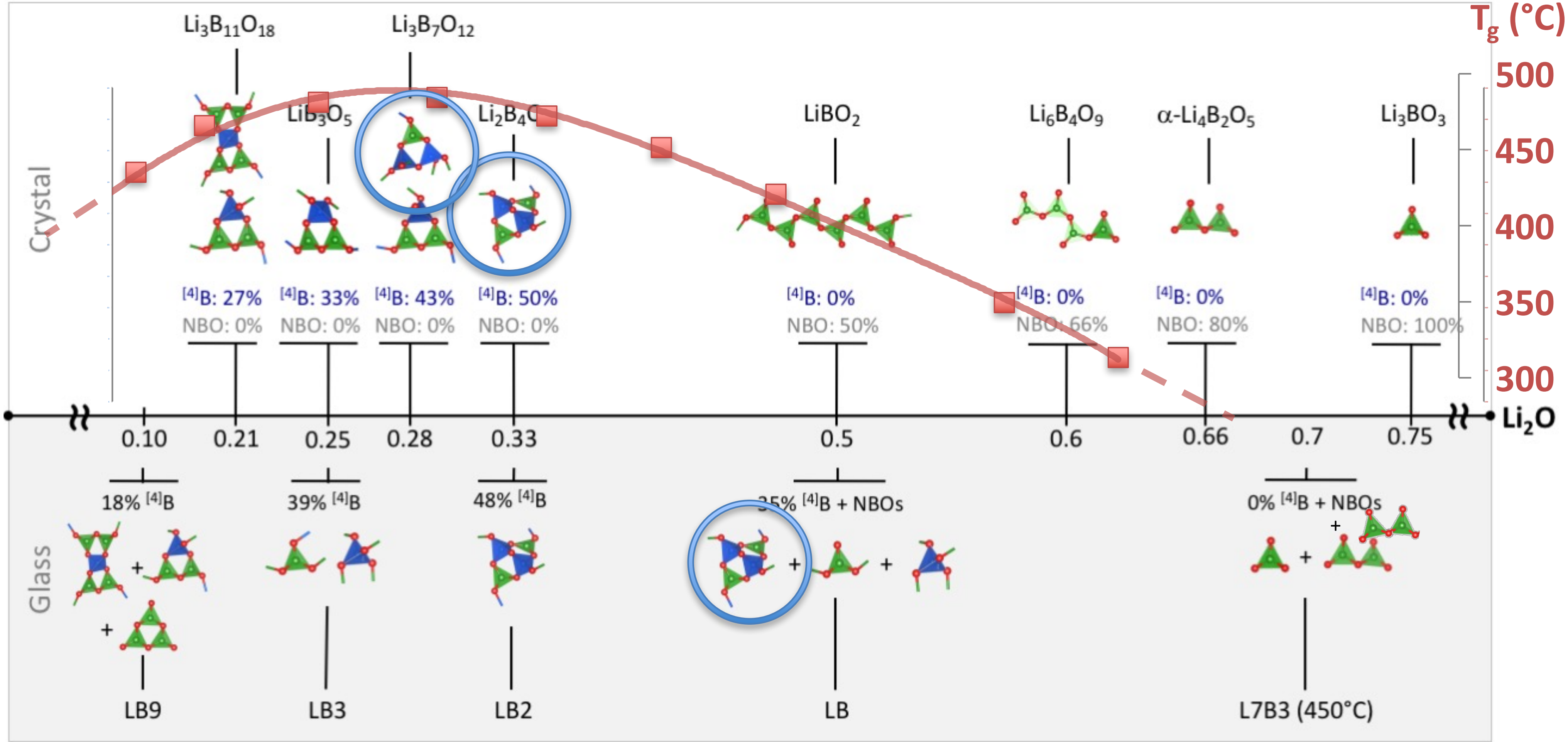
BORATE ANOMALIES …



Similarities glass ⟷cristal at the local scale

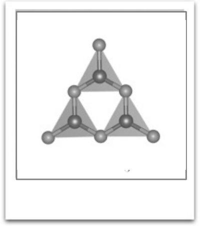
Discrepancies in the local structure of glass & cristal

BORATE ANOMALIES ...



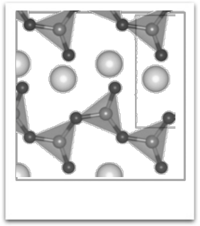
Important role of the superstructural units (medium range order)

OUTLINE



B_2O_3 glass

Archetypal glass former

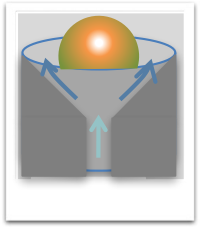


Alkali borate glasses (Li, Na, K, Rb, Cs)

Vitrification domains

Alkali effects on physical properties

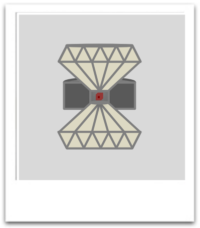
Glass structure: short- and intermediate-range order



From glass to melt

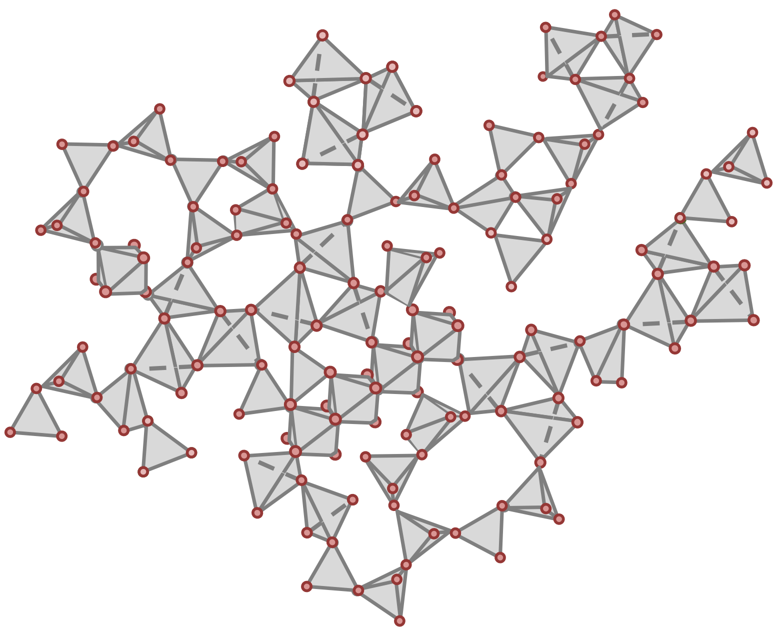
Structure of alkali borate melts

Depolymerization of the borate network

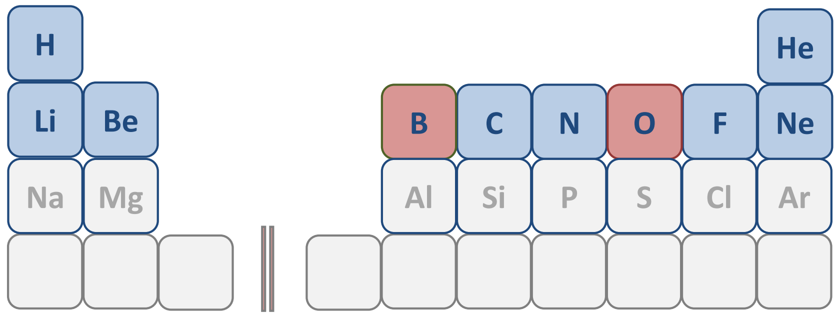


Polyamorphism

Borate glasses - low Z elements



PERIODIC TABLE OF ELEMENTS

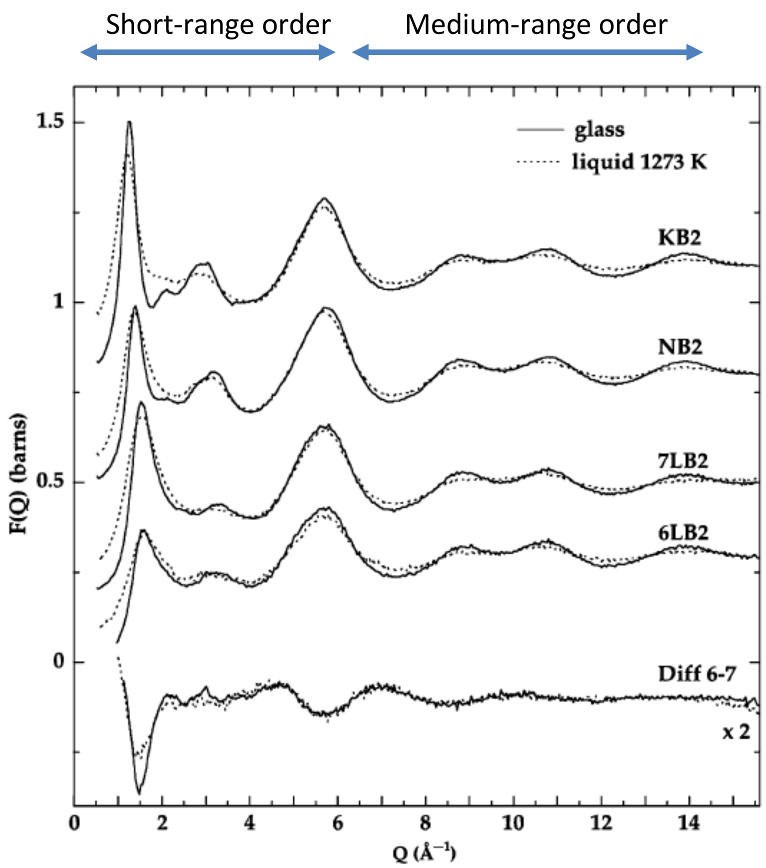


⇒ Tractable when working at ambient conditions (^{17}O NMR, Soft X-ray XANES, ND, EELS, …)

⇒ Much more complex problem under extreme conditions (HP/HT)

STRUCTURE OF BORATES VS. TEMPERATURE

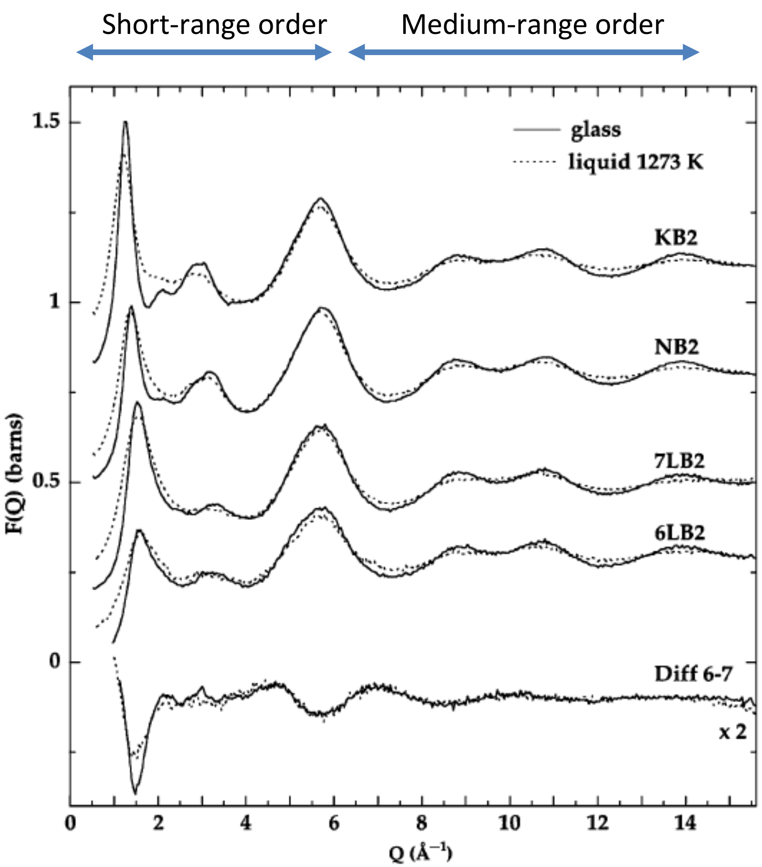
NEUTRON DIFFRACTION



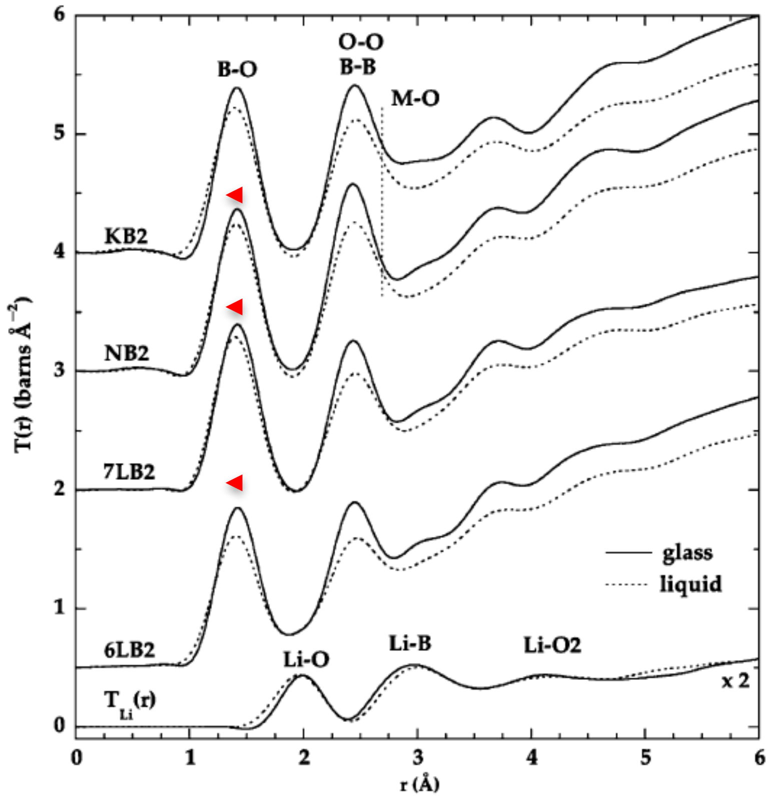
Cormier et al. JACS 89, 13-19 (2006)

STRUCTURE OF BORATES VS. TEMPERATURE

NEUTRON DIFFRACTION



Total Structure Factor

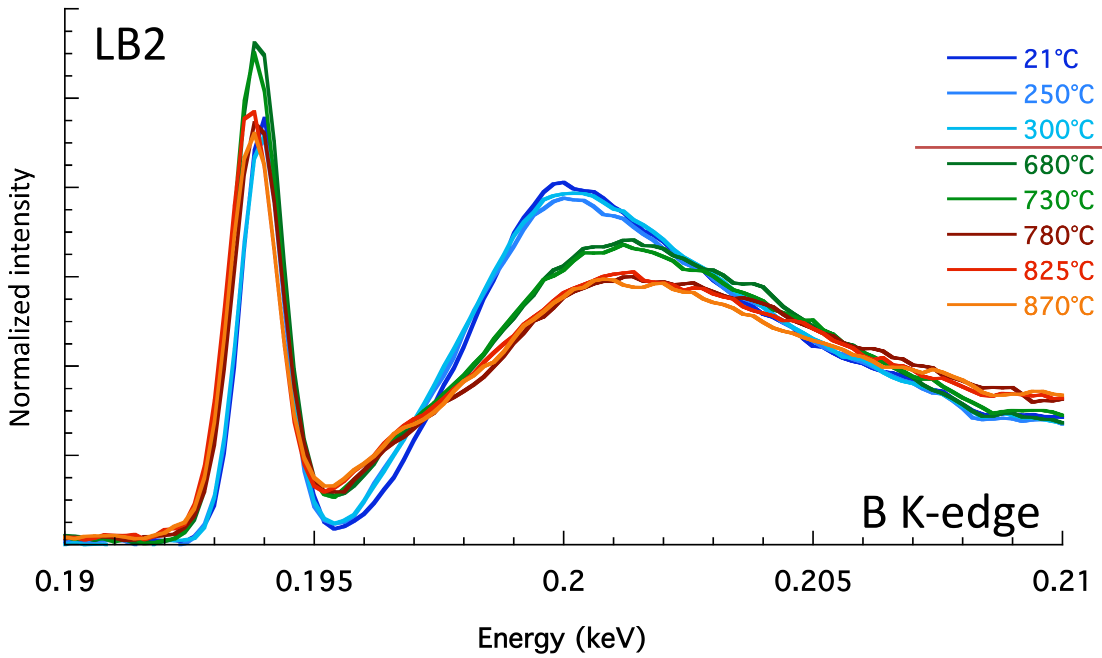


Total Correlation Function

Cormier et al. JACS 89, 13-19 (2006)

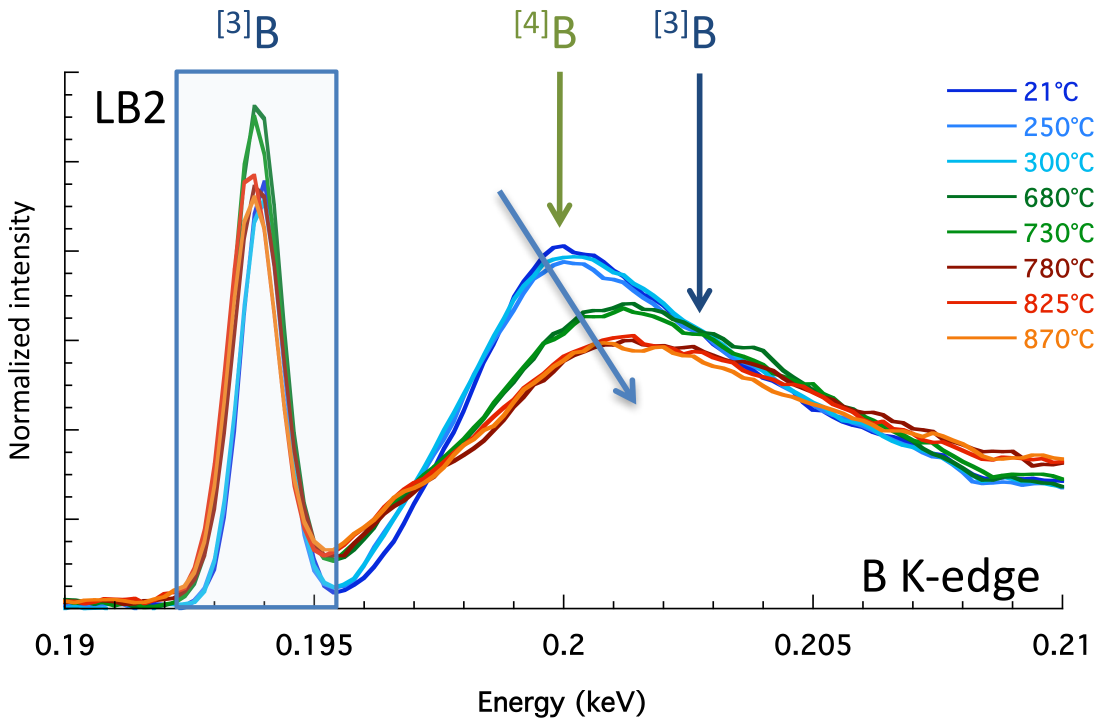
LITHIUM BORATES VS TEMPERATURE

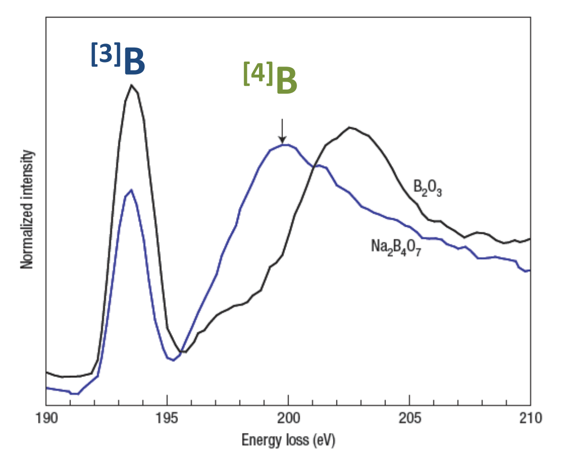
NRIXS ≈ XAS at B K-edge



$T_g = 500°C$

LITHIUM BORATES VS TEMPERATURE





Lee *et al.*, Nature materials (2005) 4, 851-854.

There is a conversion [4]B → [3]B during the heating

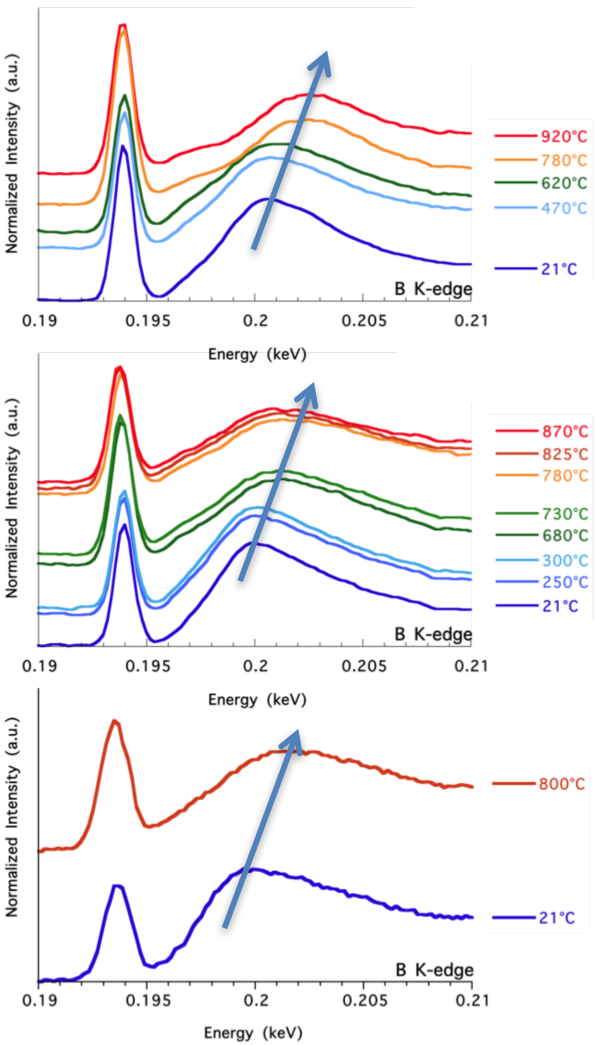
O K-EDGE OF LI BORATES VS TEMPERATURE

B K-edge

LB3

LB2

LB



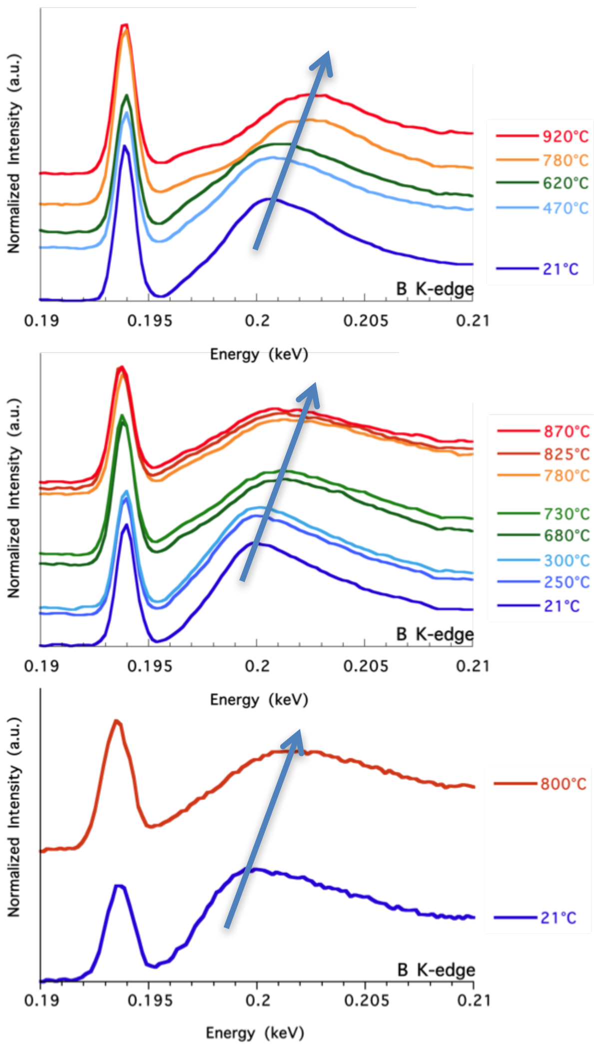
O K-edge NRIXS of Li borates vs temperature

B K-edge

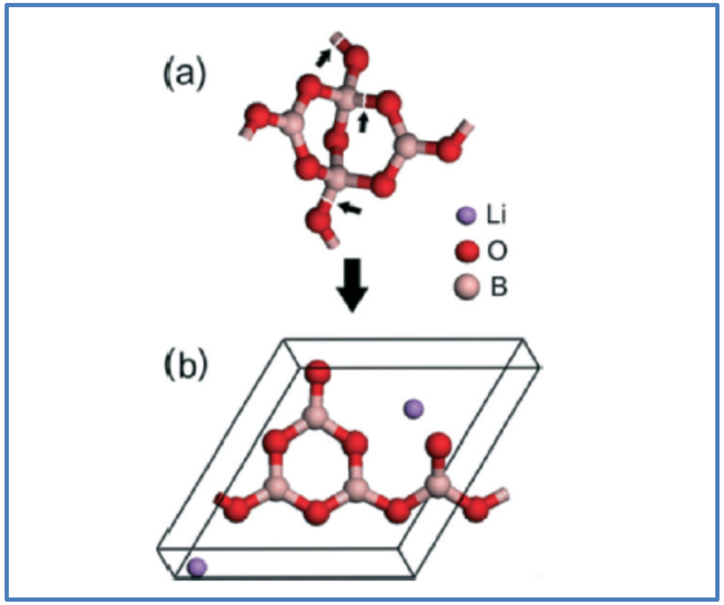
LB3

LB2

LB

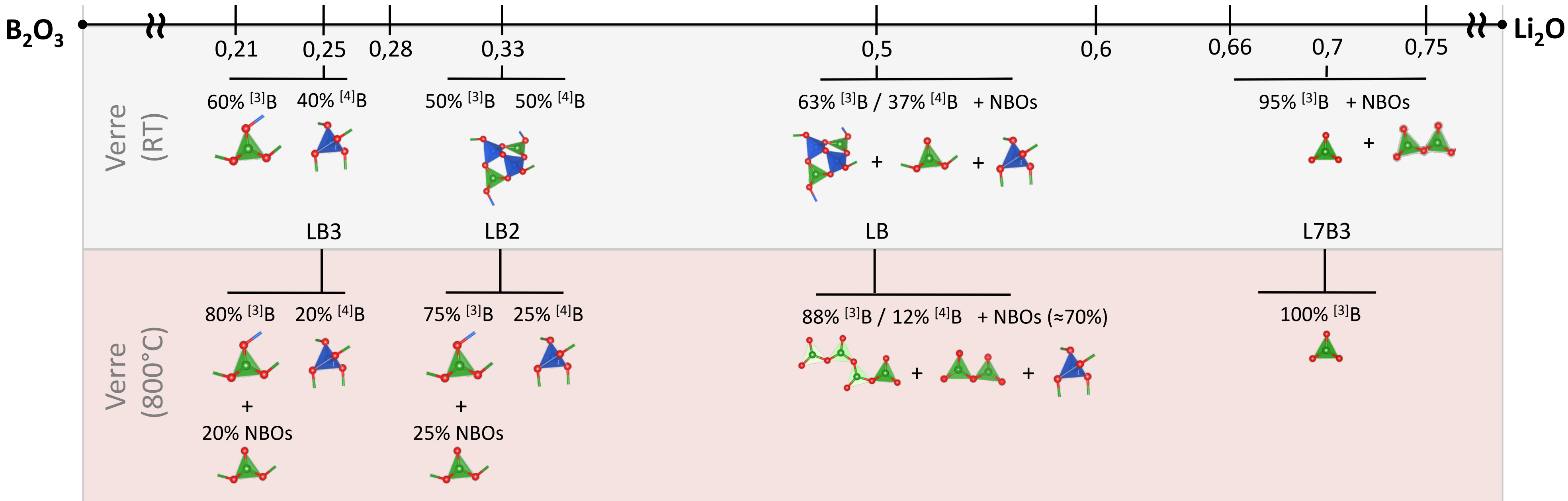


Wan et al. Cryst. Eng. Comm. 2014

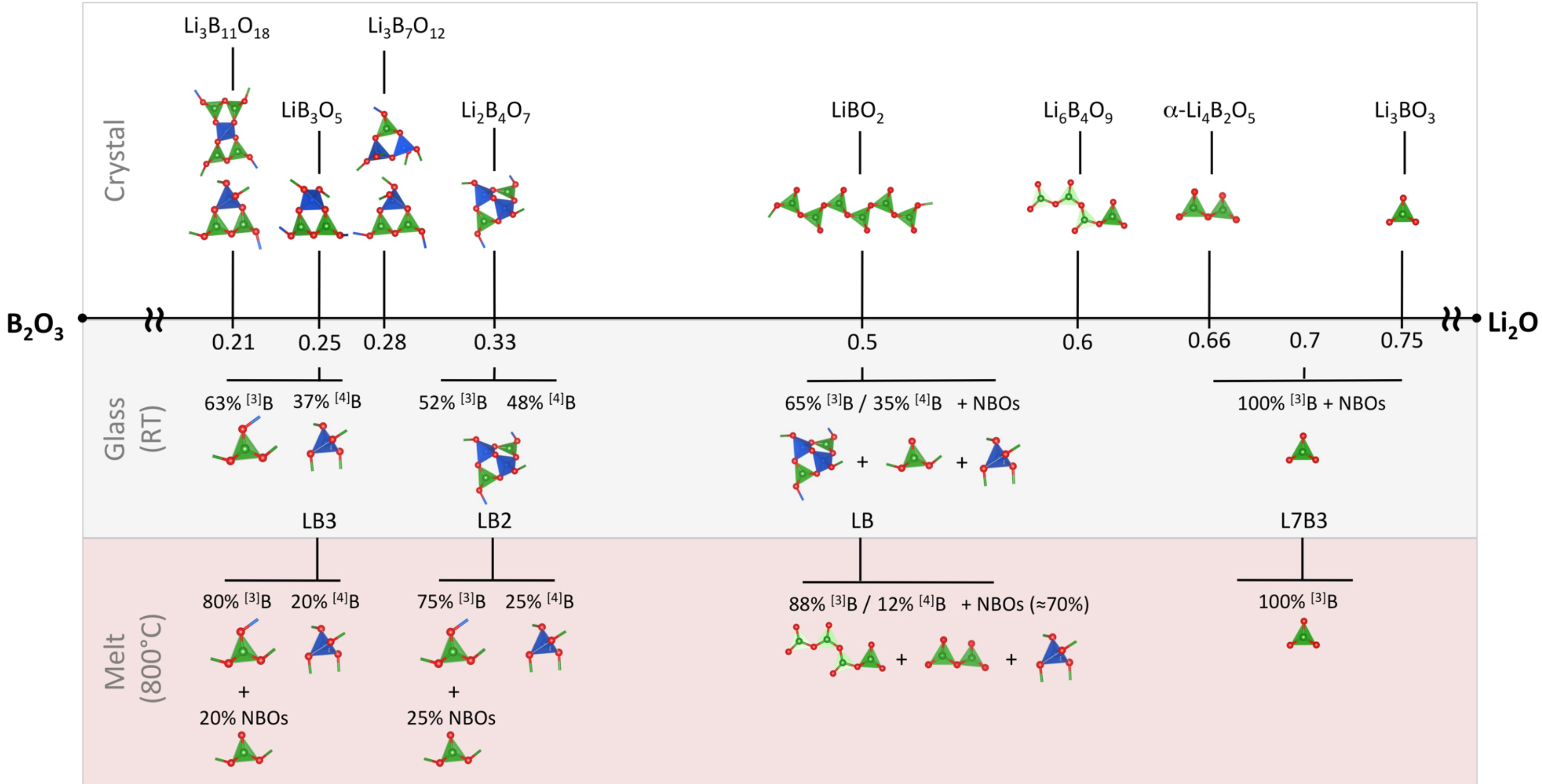


GLASS VS MELT….

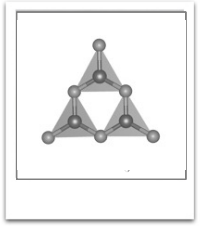
- Increasing temperature has a large impact on :
  - N_4
  - number of NBOs
  - diffusivity of alkali ion
  - density
  - configurational entropy



GLASS vs CRYSTAL vs MELT

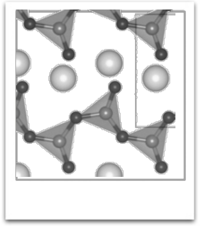


OUTLINE



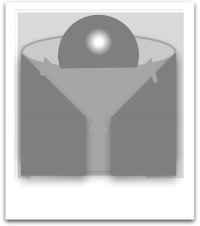
B_2O_3 glass

Archetypal glass former



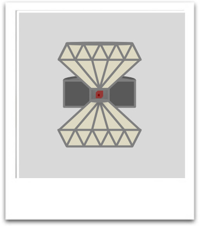
Alkali borate glasses (Li, Na, K, Rb, Cs)

Vitrification domains
Alkali effects on physical properties
Glass structure: short- and intermediate-range order



From glass to melt

Structure of alkali borate melts
Depolymerization of the borate network



Polyamorphism

POLYAMORPHISM

POLYAMORPHISM: ABILITY FOR A SYSTEM TO FORM SEVERAL DISTINCT AMORPHOUS STRUCTURES OF IDENTICAL COMPOSITION.

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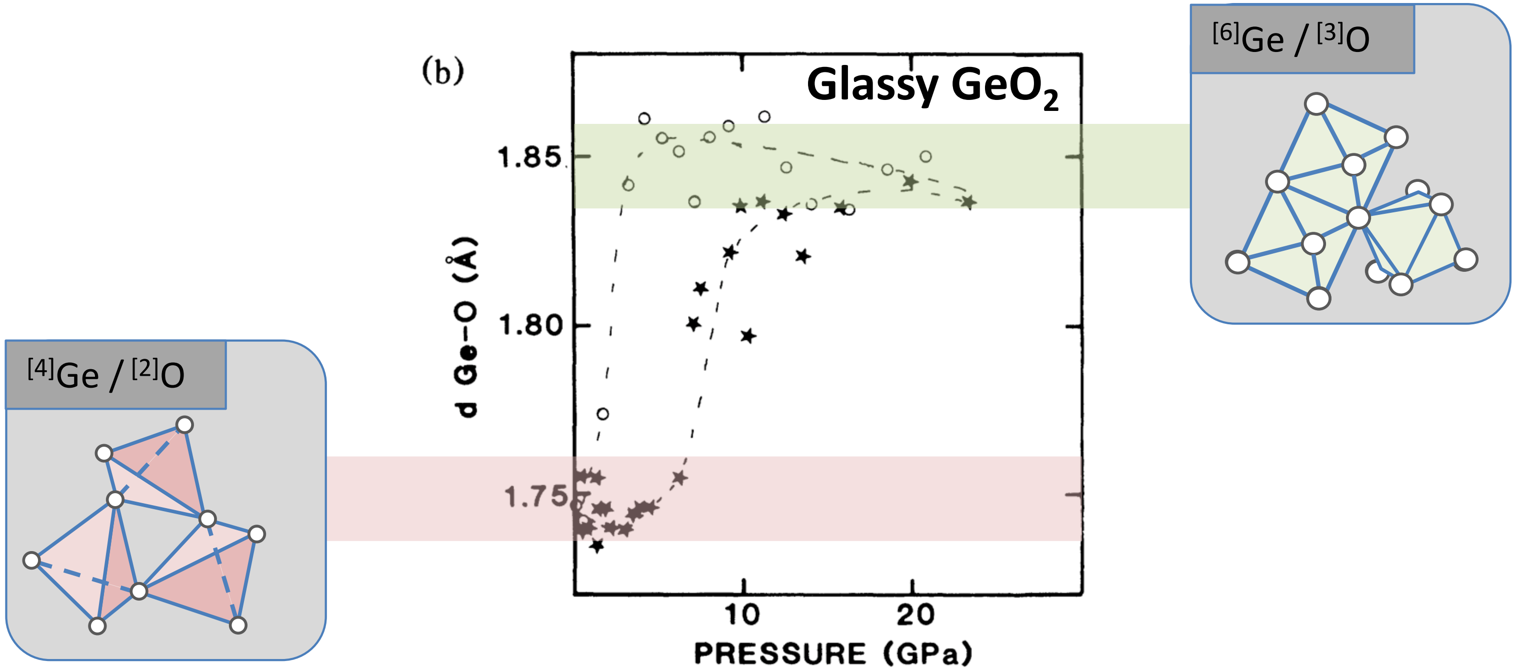
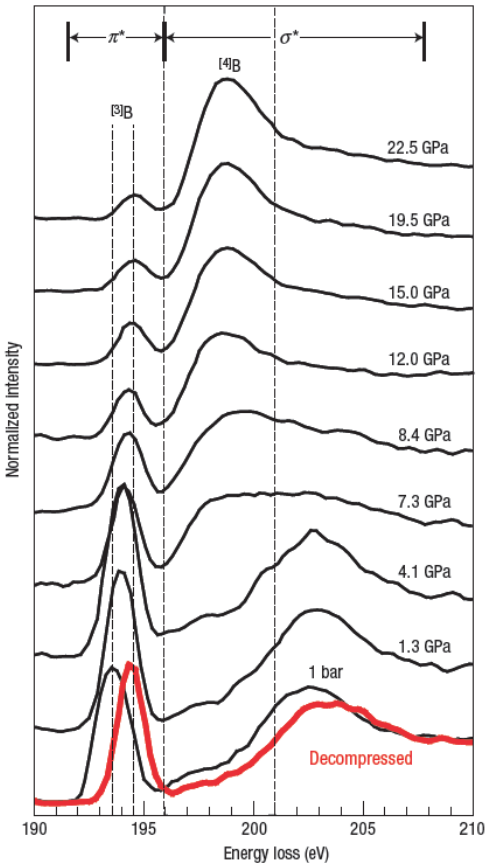


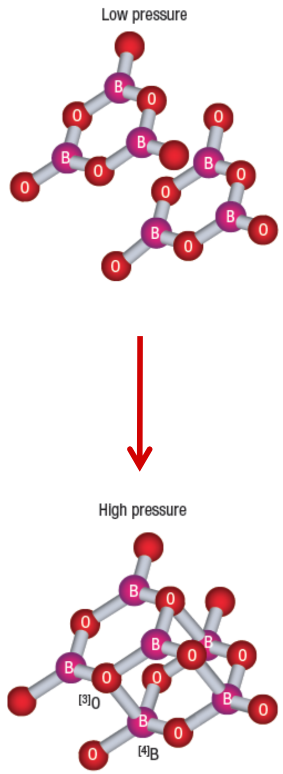
→ Four-fold to six-fold coordinated Ge atom transition

Itié et al. PRL 63, 398 (1989)

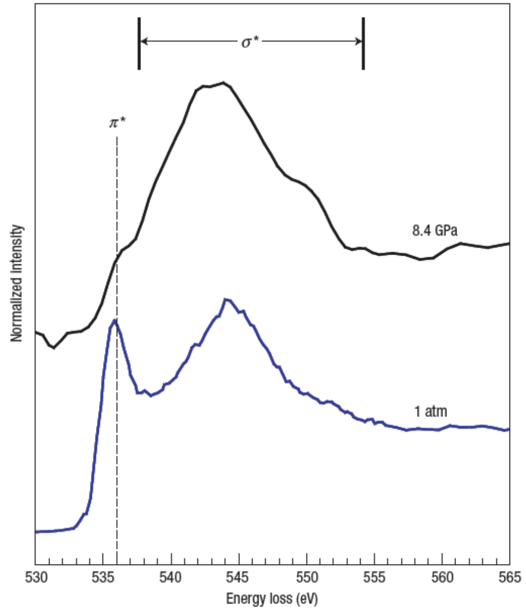
Polyamorphism in glassy B_2O_3

B K-edge



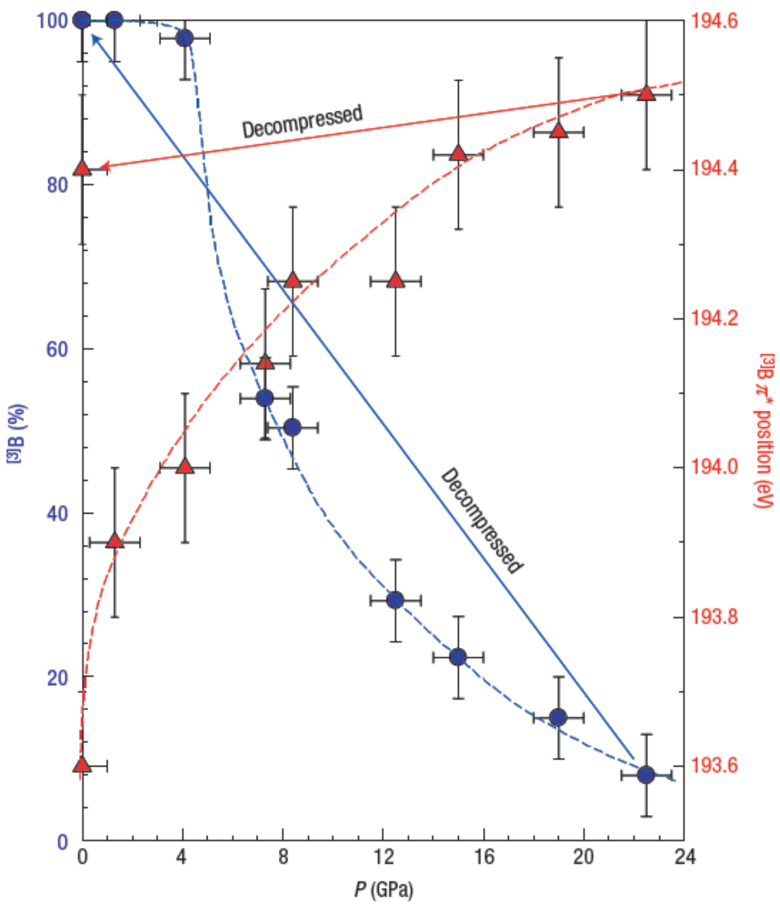


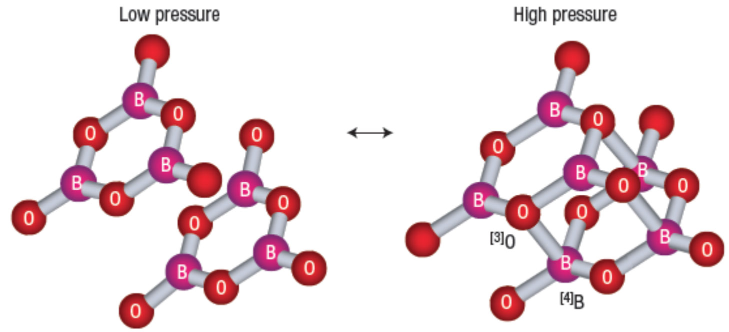
O K-edge



Lee et al. Nature Mat. 4, 851 (2005)

POLYAMORPHISM IN GLASSY B_2O_3





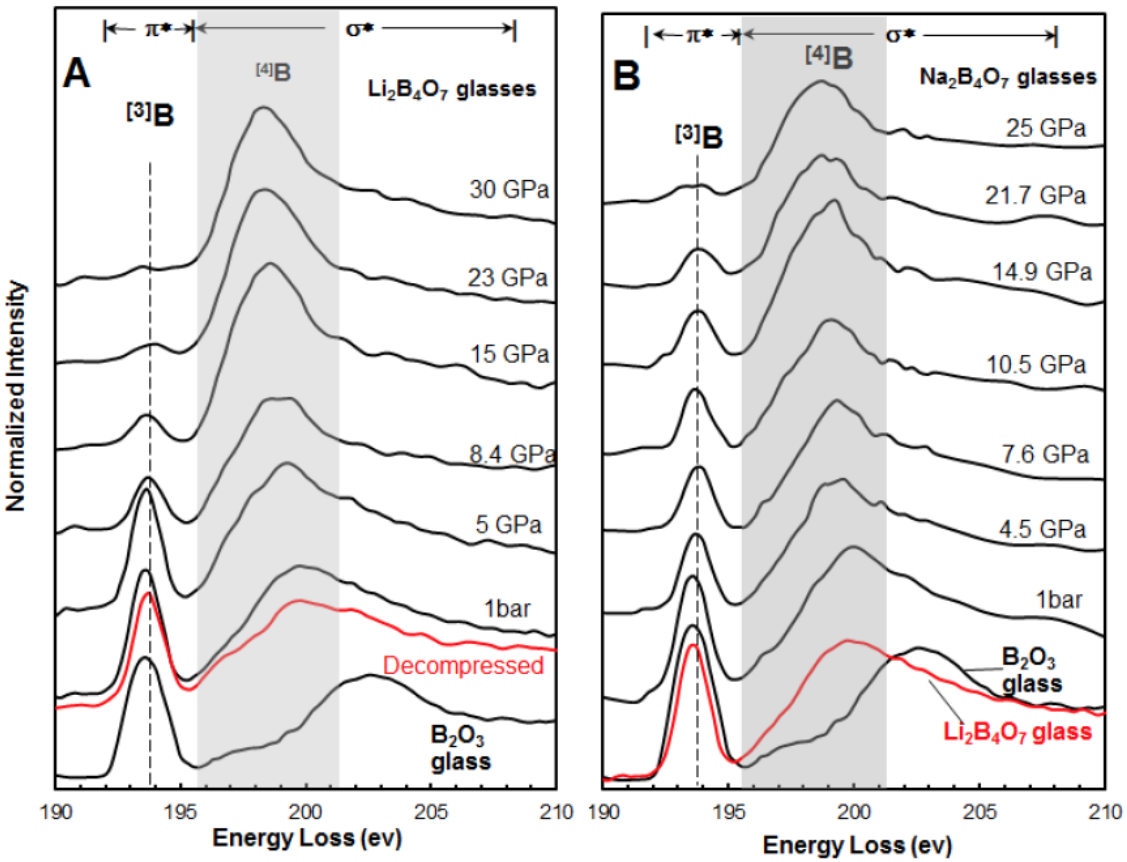
With compression:

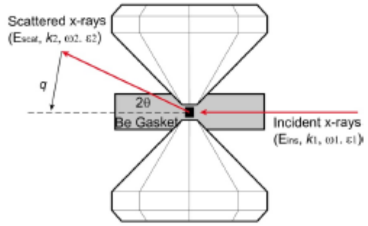
$^{[3]}B \rightarrow {}^{[4]}B$ conversion

$^{[2]}O \rightarrow {}^{[3]}O$ conversion

Lee et al. Nature Mat. 4, 851 (2005)

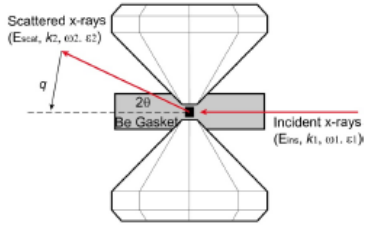
POLYAMORPHISM IN ALKALI BORATES

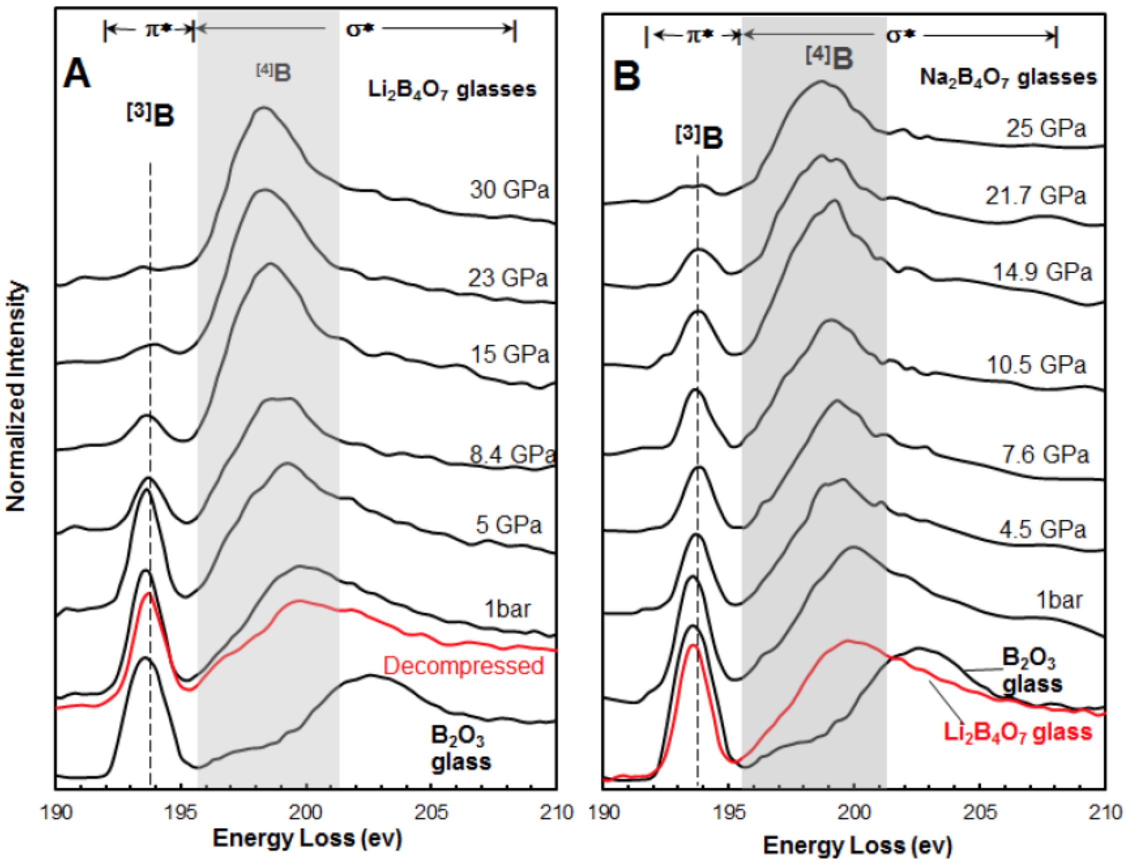


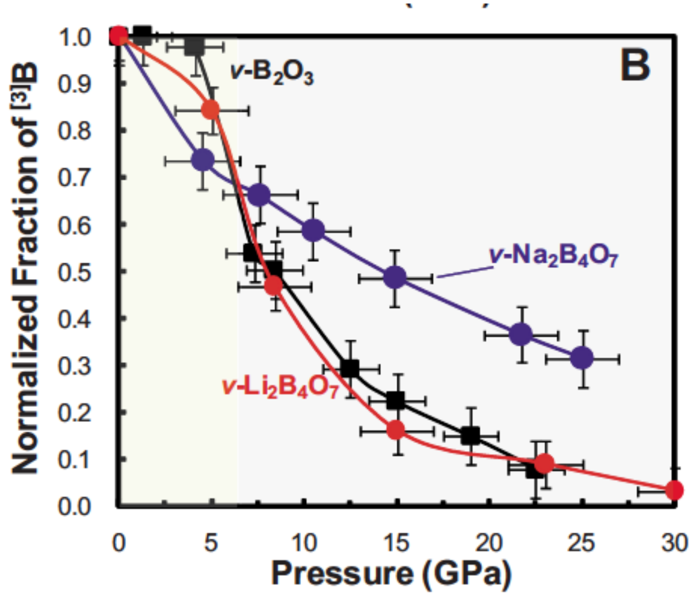


Lee et al. PRB 78, 6 (2008) / Lee et al. Rev. Mineral. Geochem. 78, 139 (2014)

POLYAMORPHISM IN ALKALI BORATES

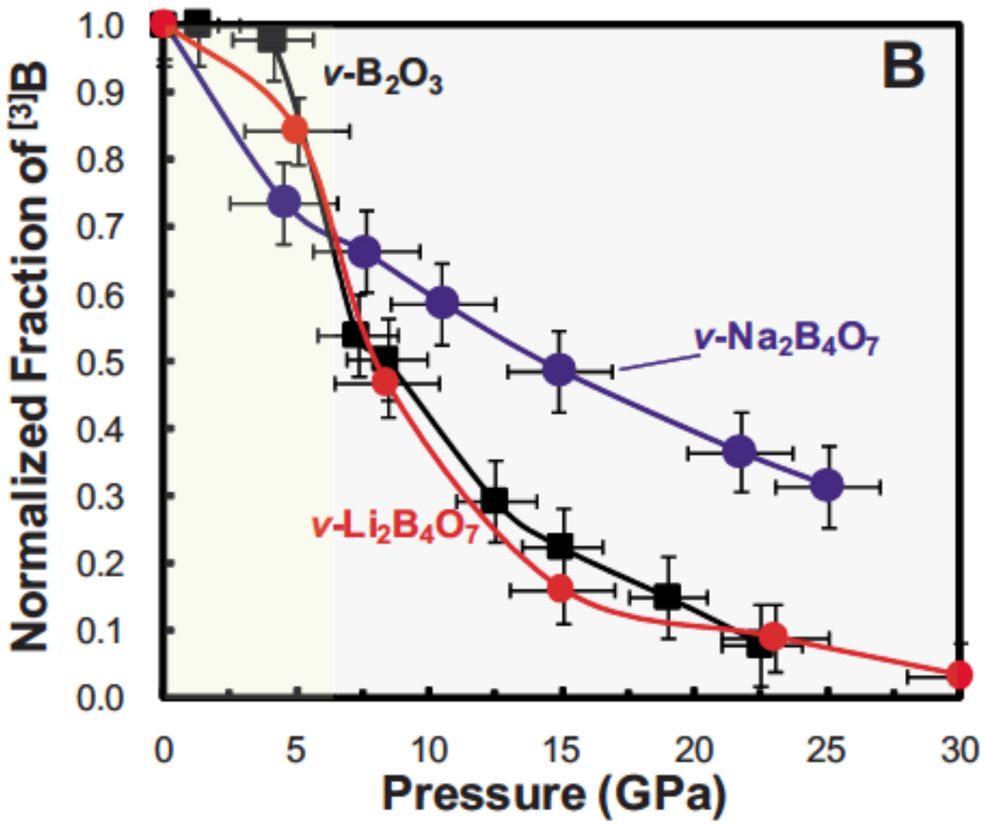






Lee et al. PRB 78, 6 (2008) / Lee et al. Rev. Mineral. Geochem. 78, 139 (2014)

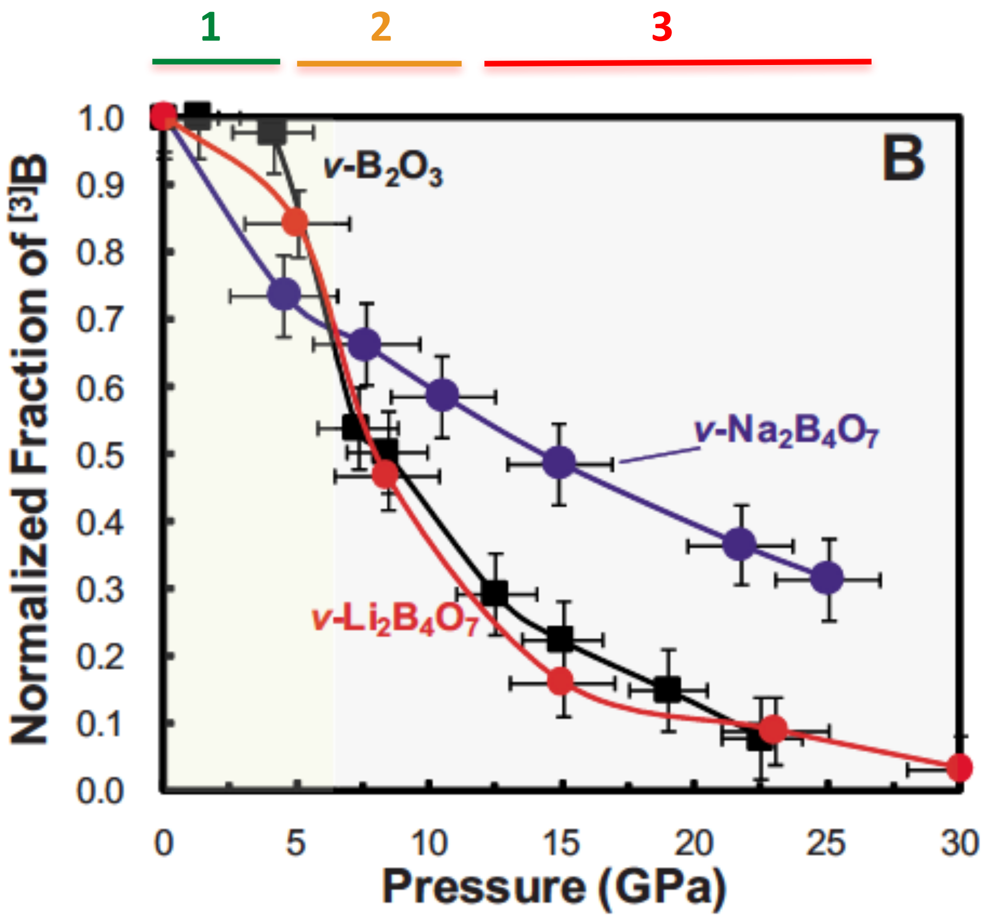
POLYAMORPHISM IN ALKALI BORATES



Lee et al. PRB 78, 6 (2008)

POLYAMORPHISM IN ALKALI BORATES

MULTI-STEP DENSIFICATION MECHANISM



1 – Topological variations
(no coordination change)

2 – Coordination change
(maximum speed of conversion)

3 – Larger energy cost of the conversion

Lee et al. PRB 78, 6 (2008)

BIBLIOGRAPHY

- **Borate structures: crystalline and vitreous**
  A.C. Wright – **Phys. Chem. Glass.** 51(1), 1-39 (2010).
- **Borate networks: Rigidity versus Dimensionality**
  A.C. Wright – **Phys. Chem. Glass.** 57(1), 1-14 (2016).
- **Borate glasses, crystals and melts**
  A.C. Wright, S.A. Feller, A.C. Hannon
  Society of Glass Technology, International Conference on Borates Glasses, Crystals and Melt, eds., Society of Glass Technology, Sheffield, 1997.