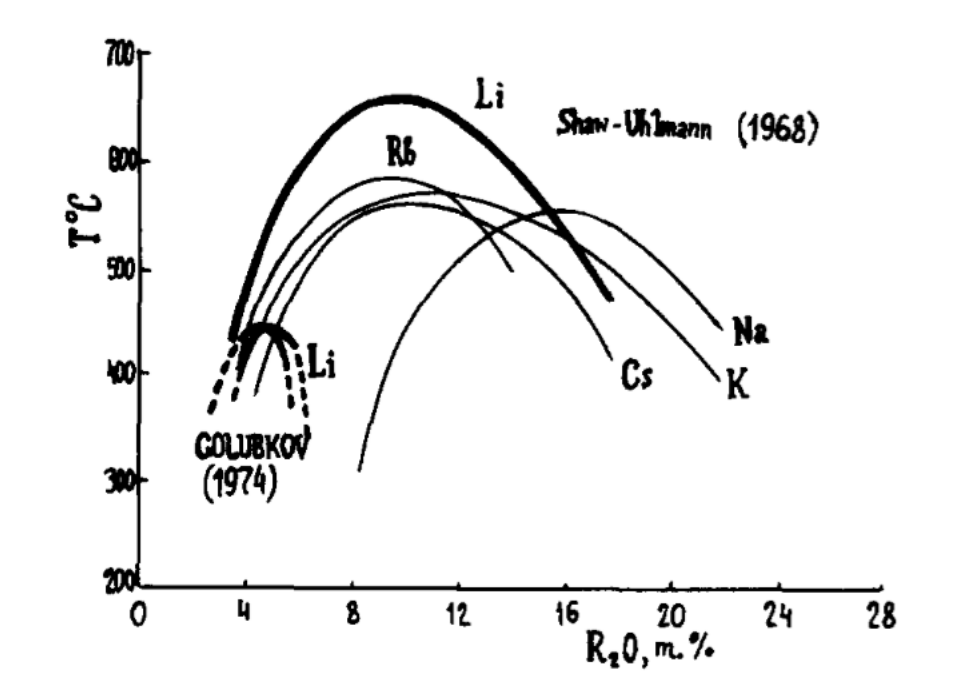
Structure des verres/liquides boratés et borosilicatés

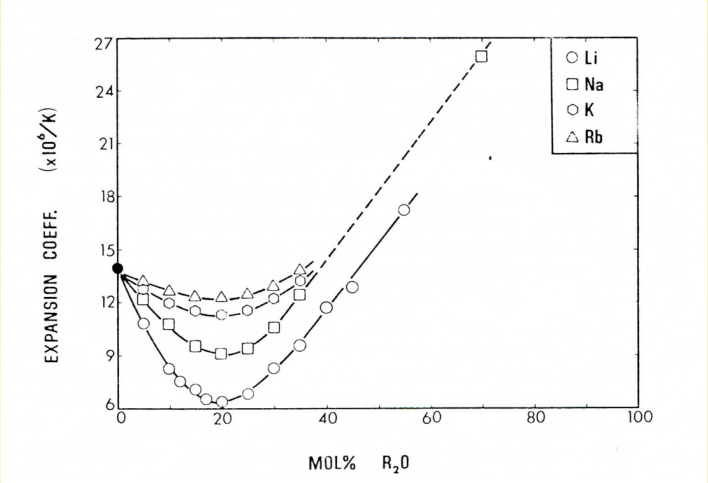
Laurent Cormier

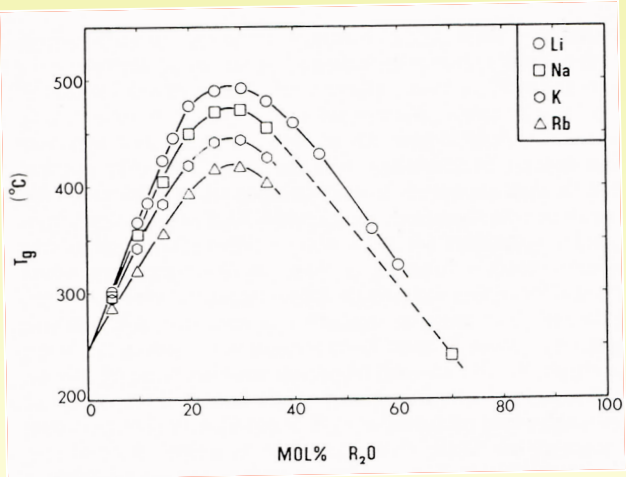
Institut de Minéralogie, Physique des Matériaux et Cosmochimie
Université Pierre et Marie Curie – CNRS
Paris, France
cormier@impmc.upmc.fr

Alkali Borate

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

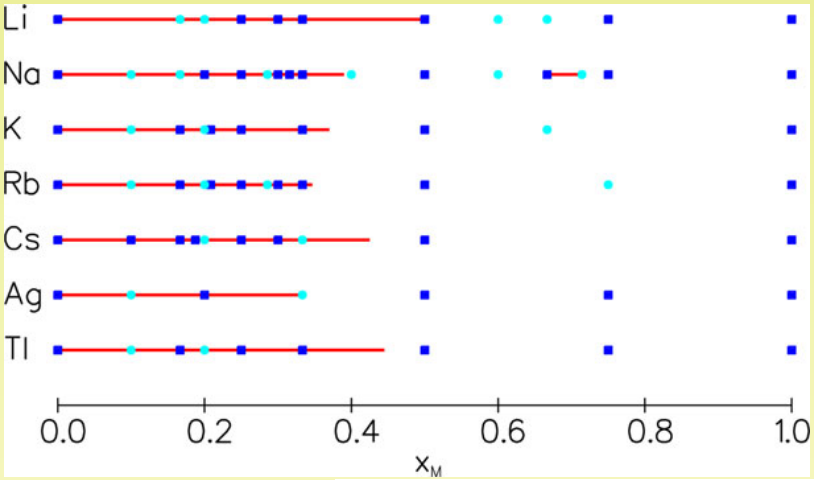


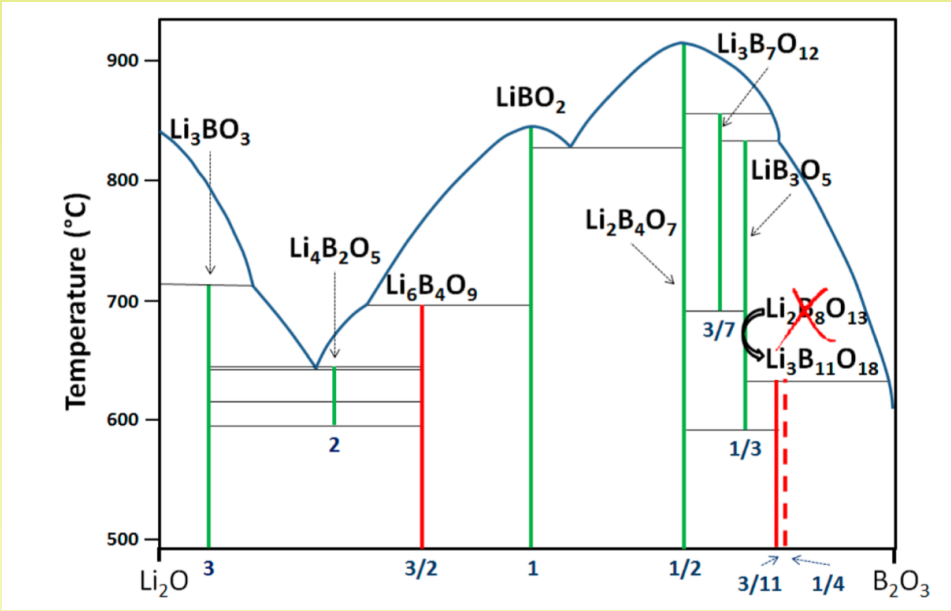


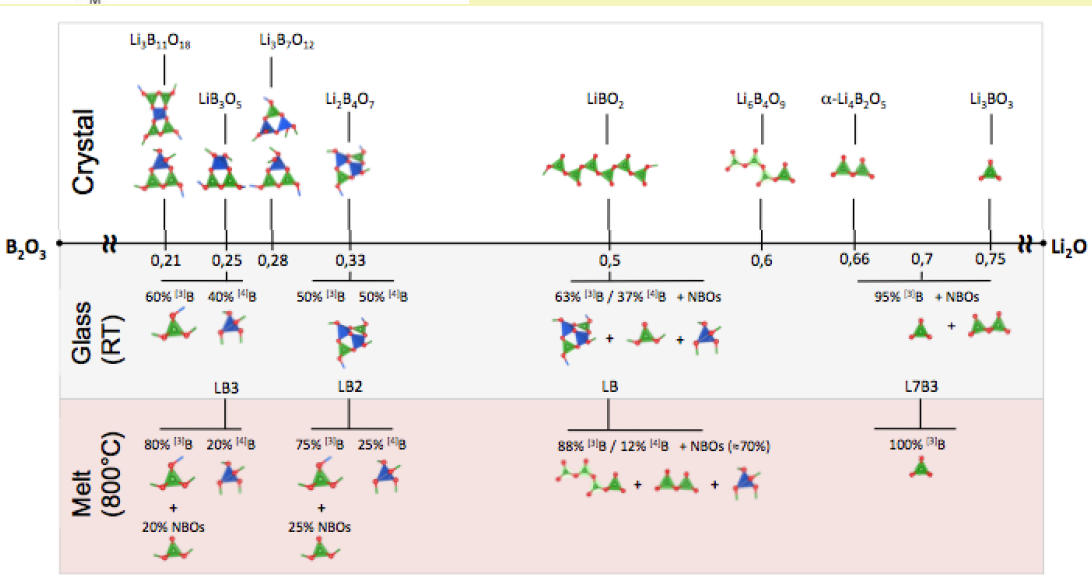


Alkali Borate

- Crystalline structures
- Glass forming regions





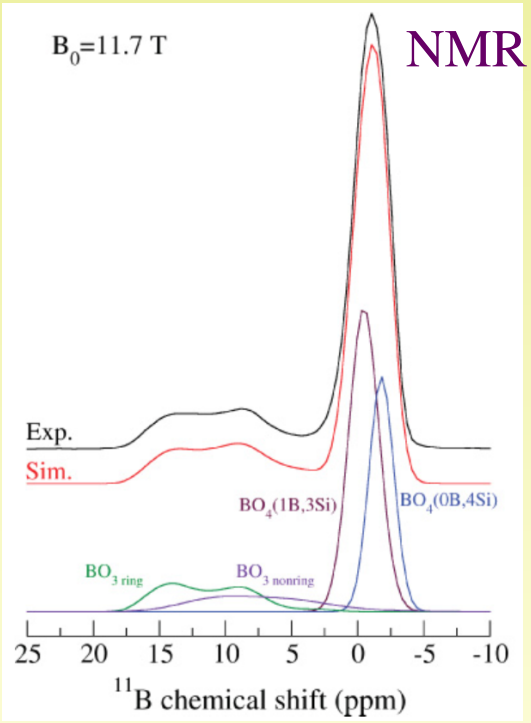


Short range order : Alkali Borate

- 2 sites for B

Triangle BO_3 - Tetrahedra BO_4^-

$d\,^3_{B\text{-}O} \approx 1.37$ Å - $d\,^4_{B\text{-}O} \approx 1.47$ Å

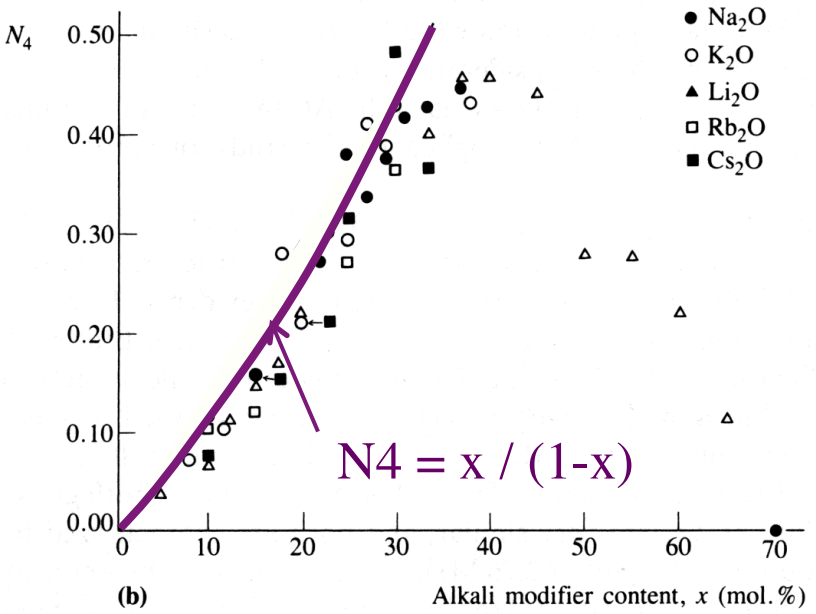


N4 = (Nbr BO_4) / (Total nbr B)

$xM_2O\ (1\text{-}x)B_2O_3$

M-BO_4 formation

NBO formation



Short range order : Alkali Borate

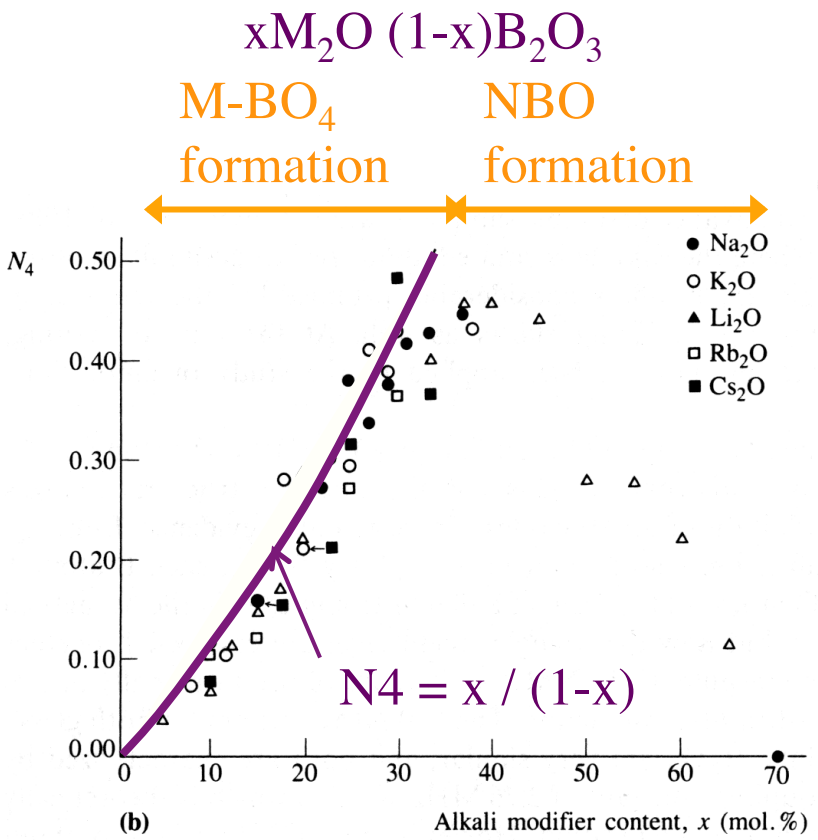
- 2 sites for B

Triangle BO_3 - Tetrahedra BO_4^-

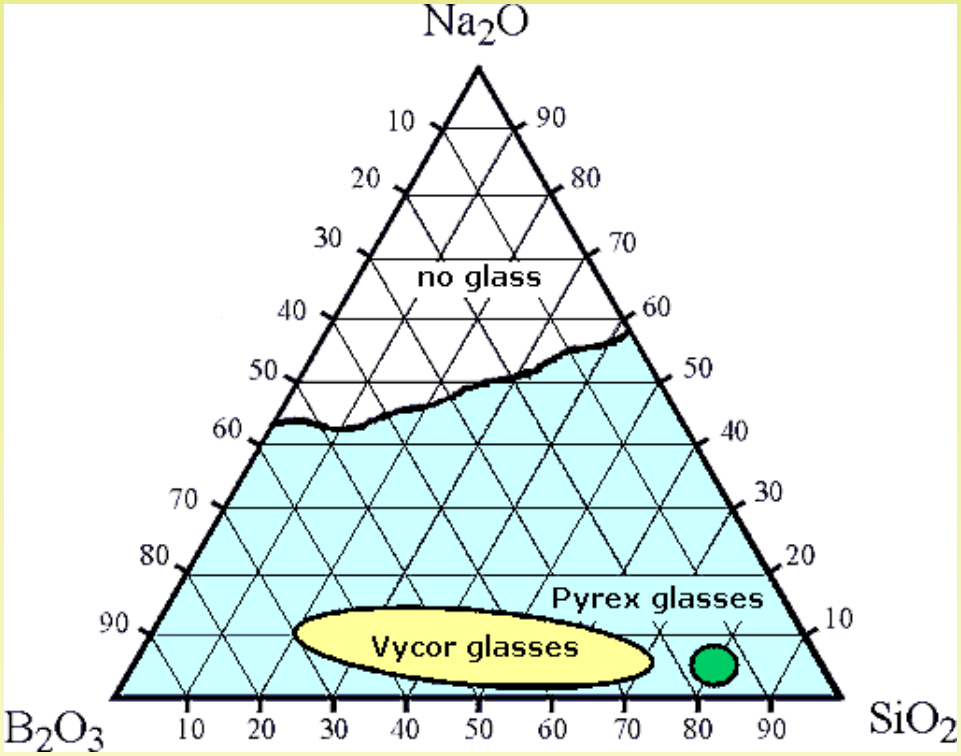
$d\,^3_{B\text{-}O} \approx 1.37$ Å - $d\,^4_{B\text{-}O} \approx 1.47$ Å

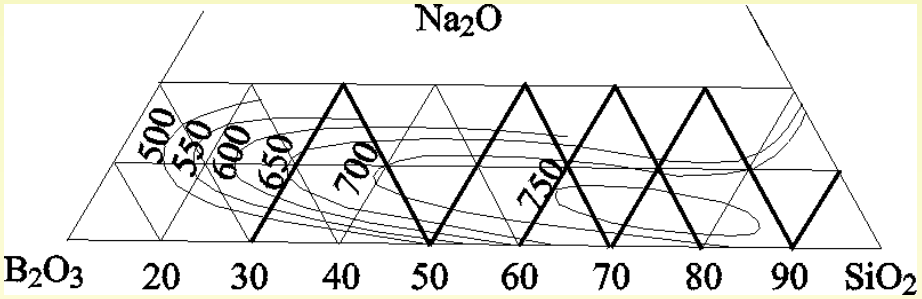
- Alkali are modifier near non-bridging oxygens (NBOs) or charge compensator near BO_4^-

⇒ Addition d'alcalins dans les borates augmentent la viscosité, Tg plus élevées ≠ silicates

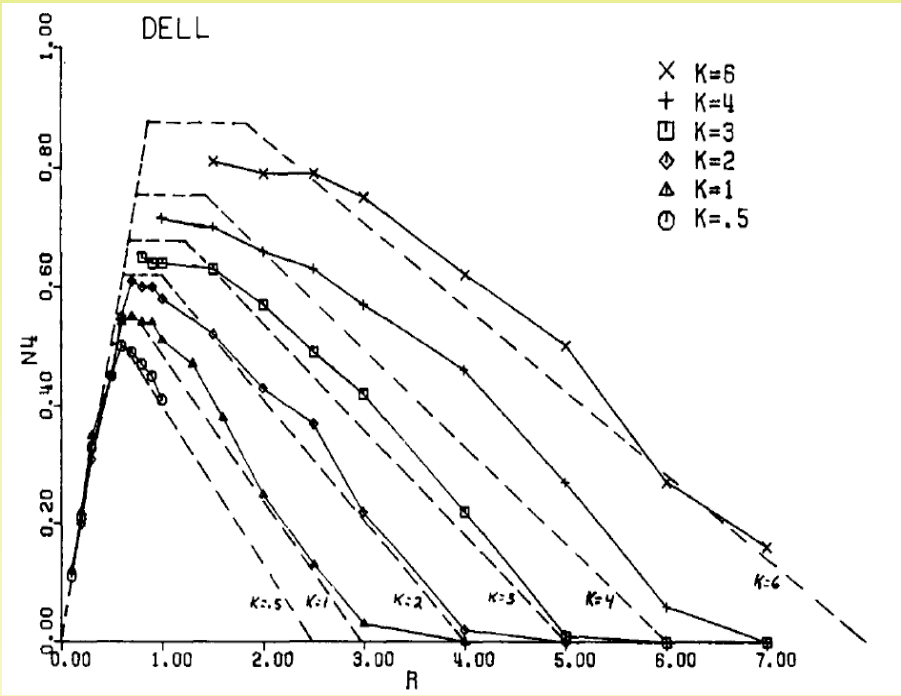


Shor rante order : Borosilicate





http://www.ptc.tugraz.at/specmag/struct/sbs.htm
Mazurin, J. Non-Cryst 95&96(1987)71

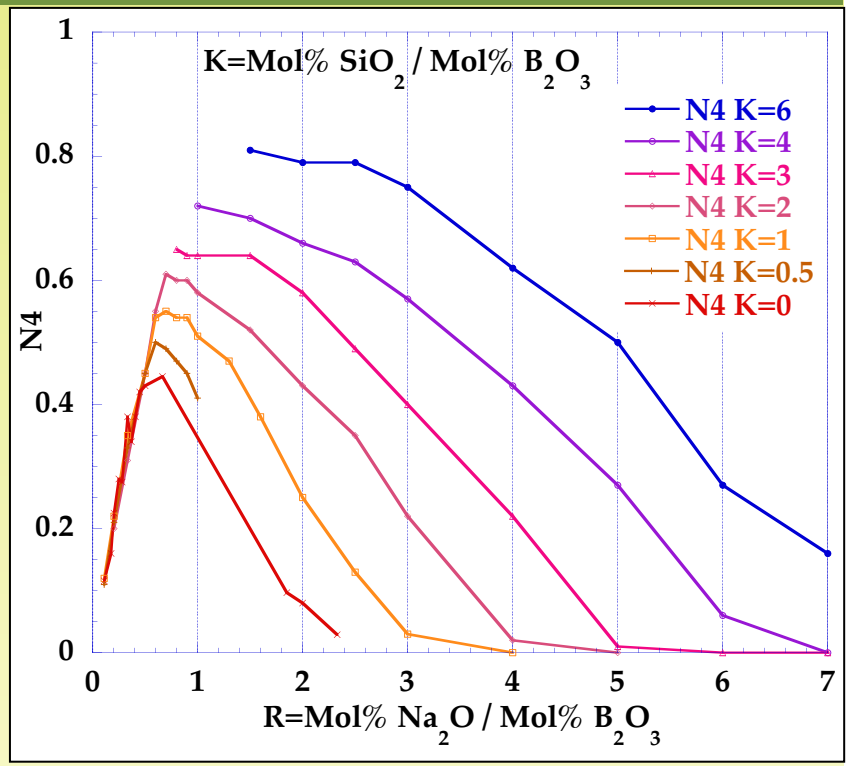


Dell, Bray and Xiao, J. Non-Cryst. Solids 58(1983)1

“Dell & Bray” model

$$R = \frac{Na_2O}{B_2O_3}$$

$$K = \frac{SiO_2}{B_2O_3}$$



first stage of creating NBOs :
ROSiØ$_3$ unit or the ROBØ$_2$ unit, or both ?

BO_4 formation

NBO formation

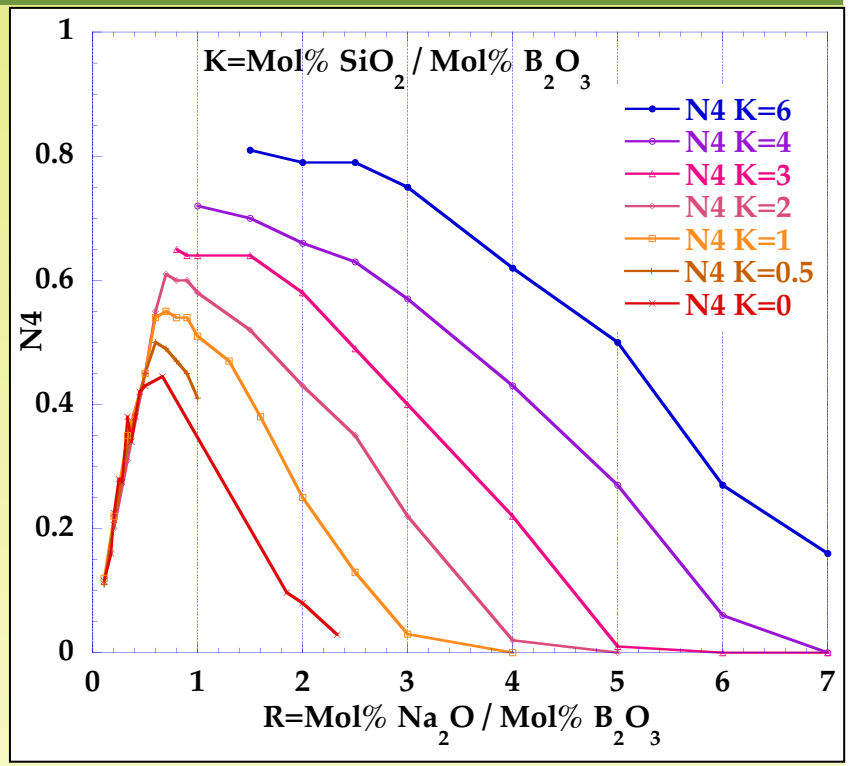
N_4 value relative to R and K

“Dell & Bray” model

Saturation of the silicate network by BO_4 units before formation of NBOs

⇒In fact important Si/B mixing and more random distribution of akalis
⇒Revision of the « Dell & Bray » model

Miura et al. J. Non-Cryst. Solids 290(2001)1
Martens & Müller-Warmuth J. Non-Cryst. Solids 265(2000) 167
Zhao et al. J. Non-Cryst Solids 276(2000)122
Manara et al. J. Non-Cryst. Solids 355(2009)2528



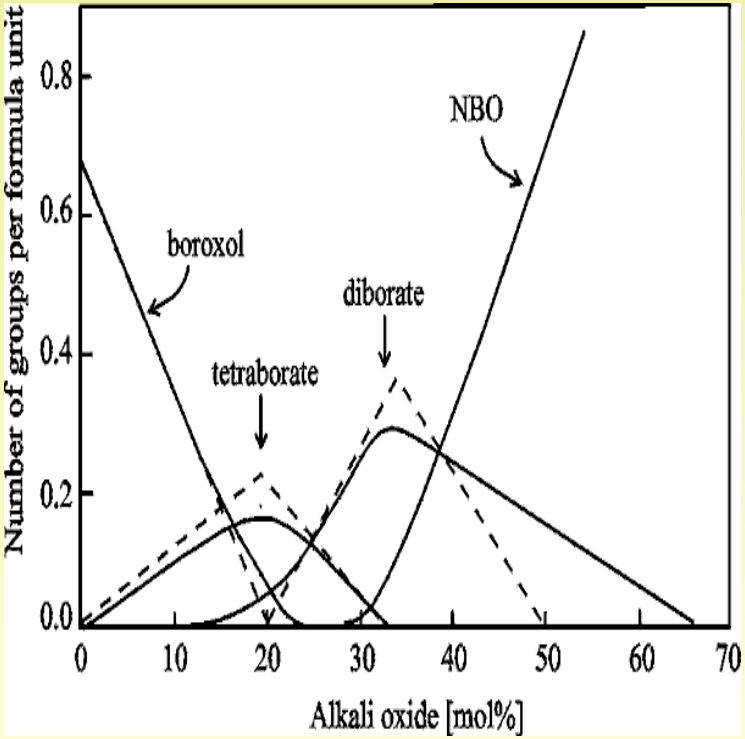
BO_4 formation

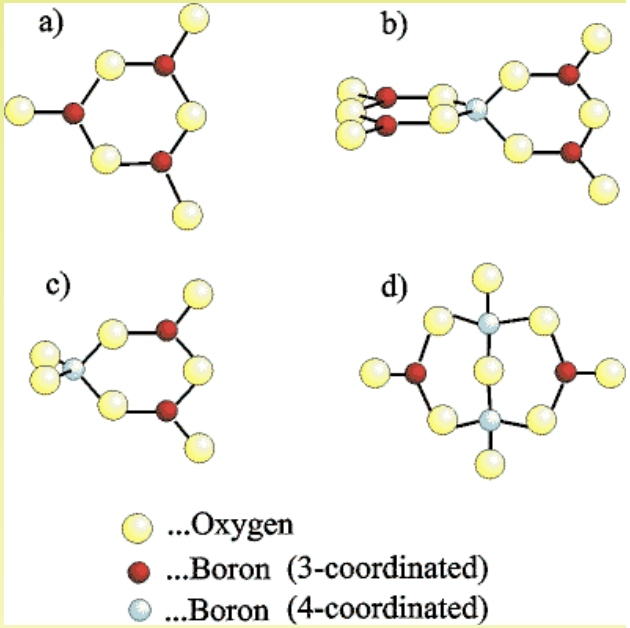
NBO formation

Medium range order : Alkali borate

- « superstructural » units

Rigid arrangements of basic units extending over medium range distances

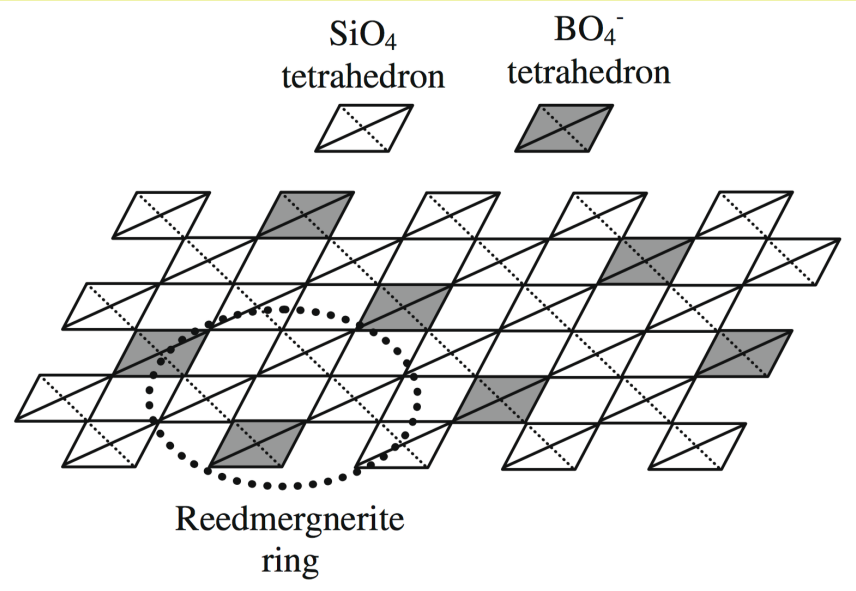




Specific vibrational modes
=> Raman

Medium range order : Borosilicate

- Reedmergnerite ring

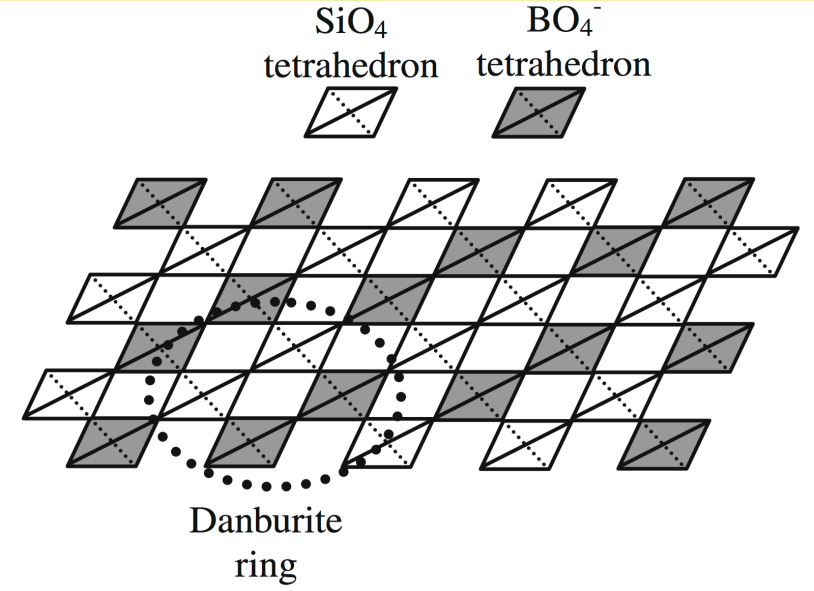


Proposed in the Dell & Bray model
Not well supported by NMR

Du & Stebbins J. Phys. Chem. B 107(2003)10063
Martens & Müller-Warmuth J. Non-Cryst. Solids 265(2000) 167
Wang & Stebbins JACerS 82(1999)1519

Medium range order : Borosilicate

- Danburite ring

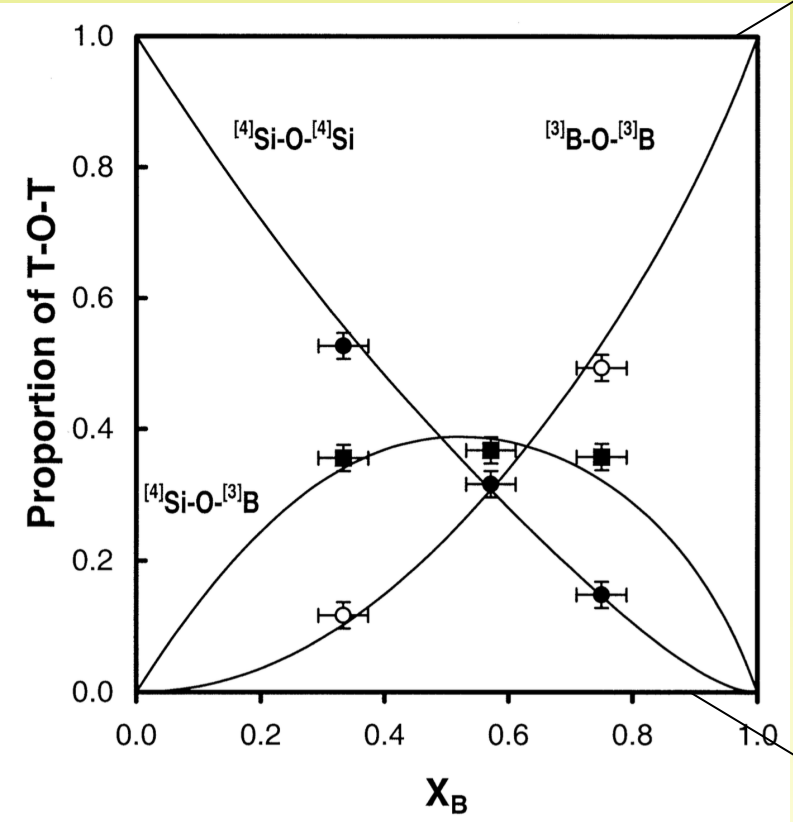


BO_4-BO_4 pairs

Bunker et al. Phys. Chem. Glasses 31(1990)30
Manara et al. J. Non-Cryst. Solids 355(2009)2528

Si/B mixing : Borosilicate

P=1 Phase separation



Degree of interdispersion

$P = 1 \exp [-(2W/kT_f(X_{Si}))$

$2W = 5.4$ kJ/mol for B_2O_3-1.5SiO_2

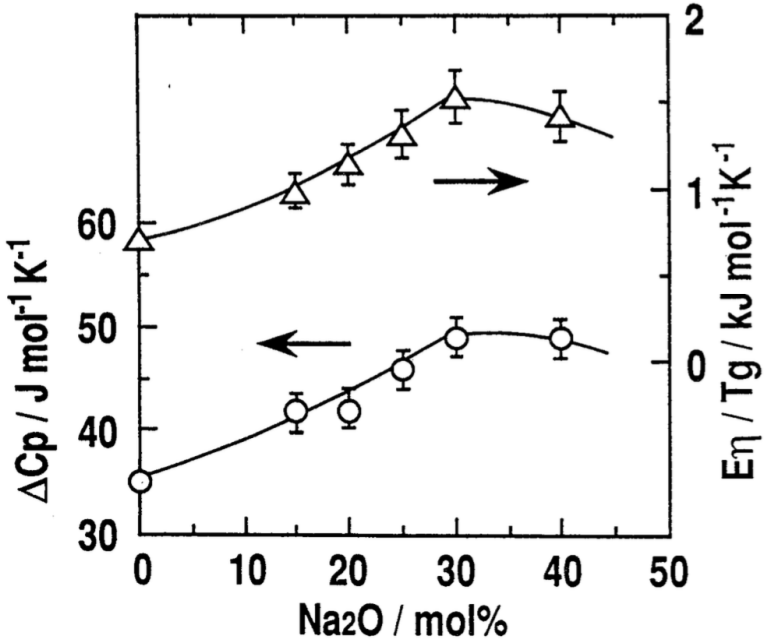
$\Rightarrow$ P~0.62

$\Rightarrow$ considerable network mixing but not fully random

P=0 Random mixing

Lee & Stebbins Geochim. Cosmochim. Acta 66(2002)303

Structural relaxation of the liquid with T (1/2)



Lee et al. J. Ceram. Soc. J. 103(1995)398

- Dynamic slowing down
- No more evolution of configuration below Tg (glass transition)

$$C_p = C_p^{vib}(T) + C_p^{conf}(T)$$

$$A\ T < T_g \Rightarrow \quad C_p^{conf}(T) = 0$$

$C_p^{conf}(T)$ more or less high according to the system

$$dH = C_p\, dT$$

Changes of configurations within the liquid

- Chemical order
- Structure

High C_p^{conf}, FRAGILE liquid

Structural relaxation of the liquid with T (2/2)

Properties

C_p^{conf}, α^{conf}, K_T^{conf}, viscosity, transport

Structural changes of the liquid

What are the structural changes that allow the liquid to remain in internal equilibrium when temperature decreases?

Do these changes take part to the glass transition phenomenon?

Network:

Basic forming units

Medium range ordering

Cationic sites:

Coordination of polyhedra

Connection to the network

Neutron structure factors for MB2 glasses

High Q range:

Short distances (BO_4, BO_3)

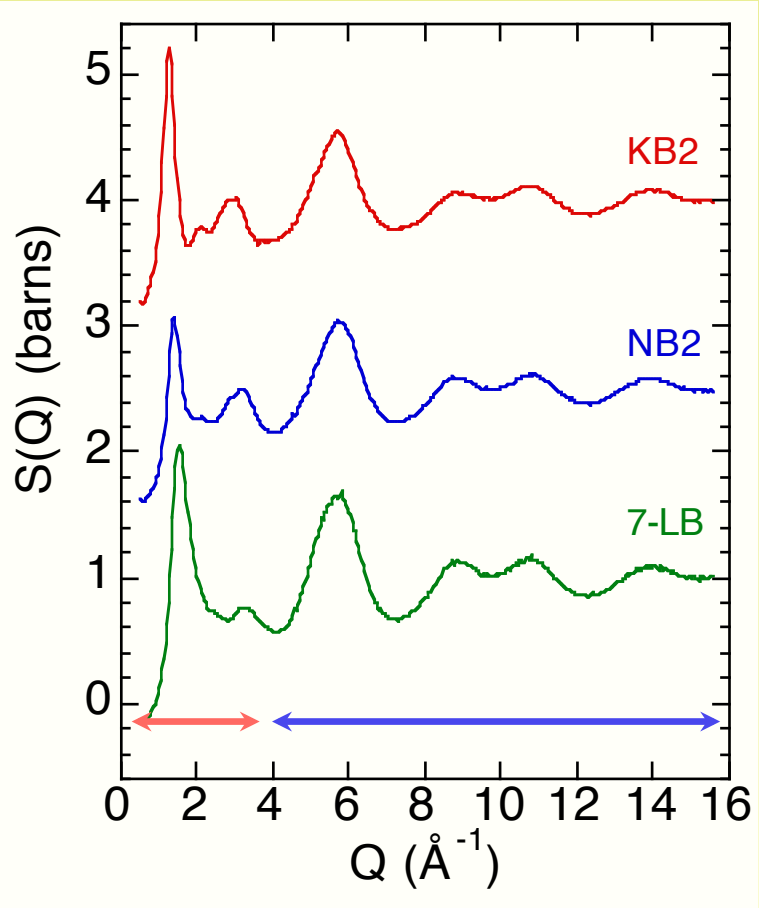
Low Q range:

Medium distances (5-8 Å)

KB2: K_2O-$2B_2O_3$

NB2: Na_2O-$2B_2O_3$

LB2: $^7Li_2O$-$2B_2O_3$



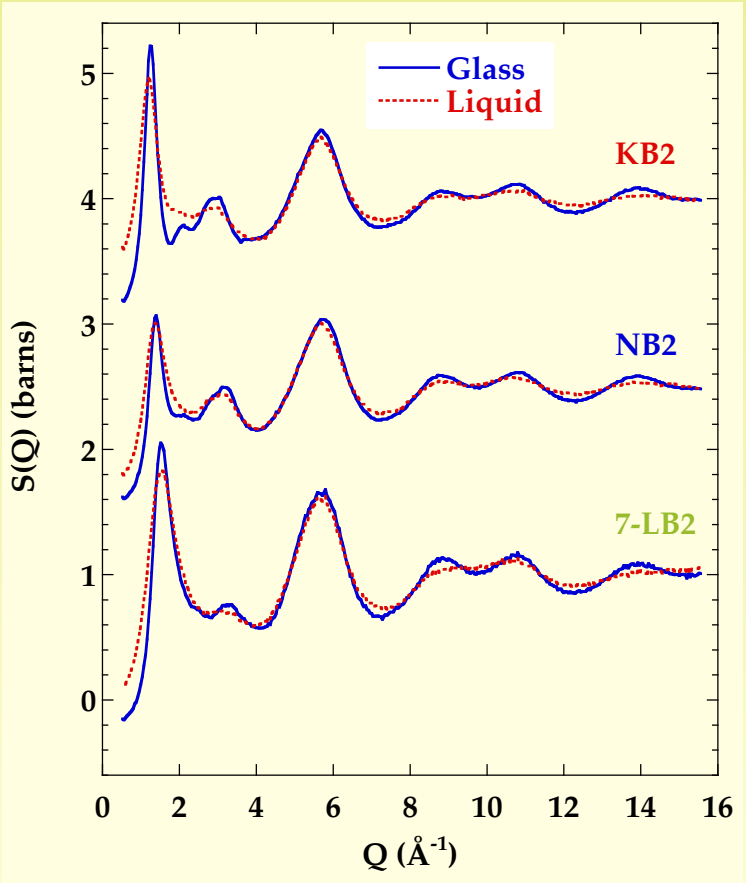
Data obtained on 7C2 diffractometer at LLB (France)

Majérus et al., Phys. Rev. B, 67 (2003) 024210

Neutron structure factors for MB2 liquids

Decrease of the amplitude of oscillations

Less structures at low Q



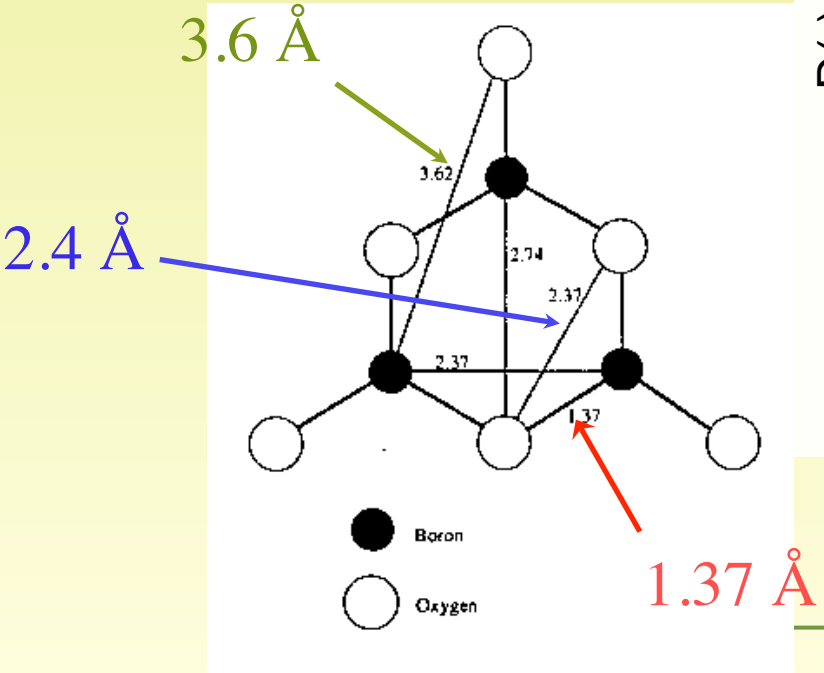
KB2: 1200 K

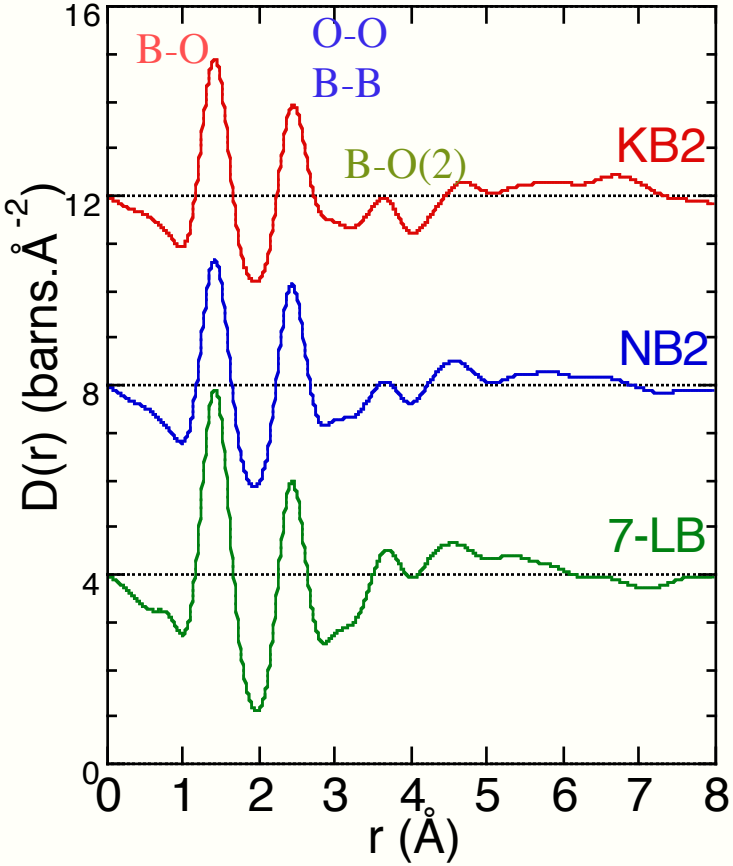
NB2: 1100 K

LB2: 1273 K

Correlation functions for MB2 glasses

First peaks due to the borate network





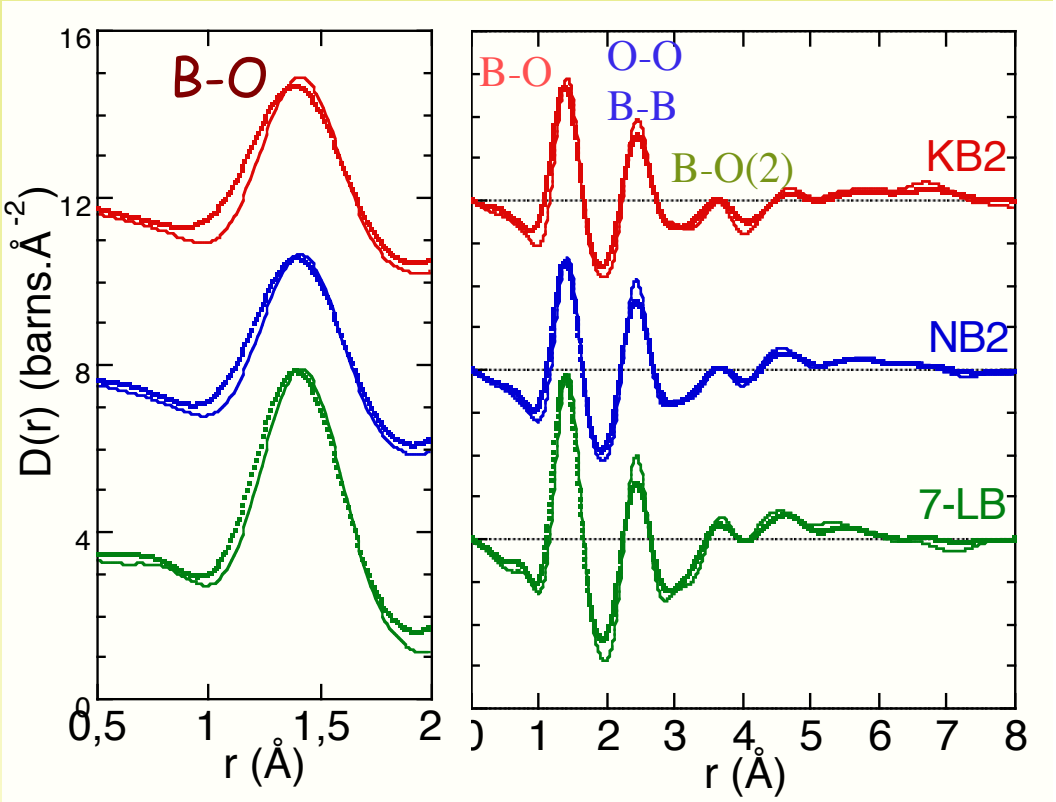
Correlation functions for MB2 liquids

Decrease in intensity of O-O peak

Disappearance of structures at 3 Å

Shift of the B-O peak by -0.01 Å

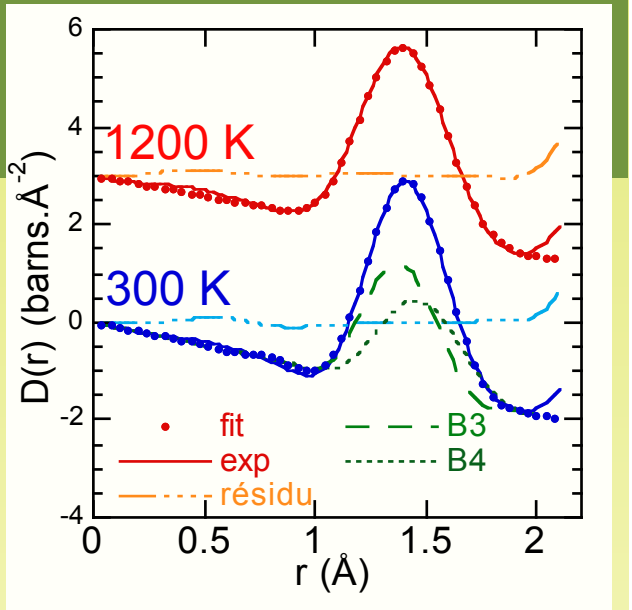
Fits with Gaussian



Triangle BO_3 - Tetrahedra BO_4^-

$d^3_{B\text{-}O} \approx 1.37$ Å - $d^4_{B\text{-}O} \approx 1.47$ Å

Fit of the B-O peak



Decrease of the proportion of BO_4^- in the liquid, by about

45 % to 30 %

Gaussian fit of the B-O peak

Fraction $BO_4/(BO_4+BO_3)$

	Verre	Liq
LB2	46	30
NB2	43	35
KB2	40	32

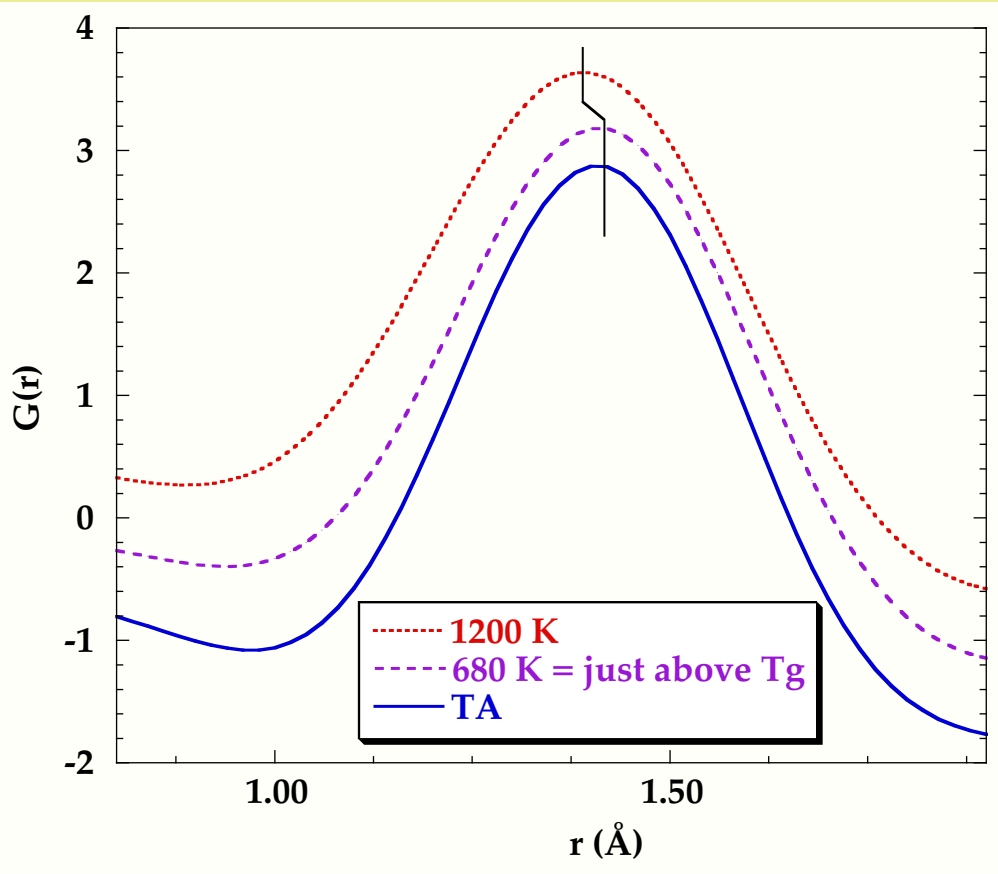
Glass → Liquid

$BO_4^- \longrightarrow BO_3 + NBO^-$

Majérus et al., Phys. Rev. B 67(2003)24210

Beginning of the BO_4 to BO_3 conversion

B-O contribution

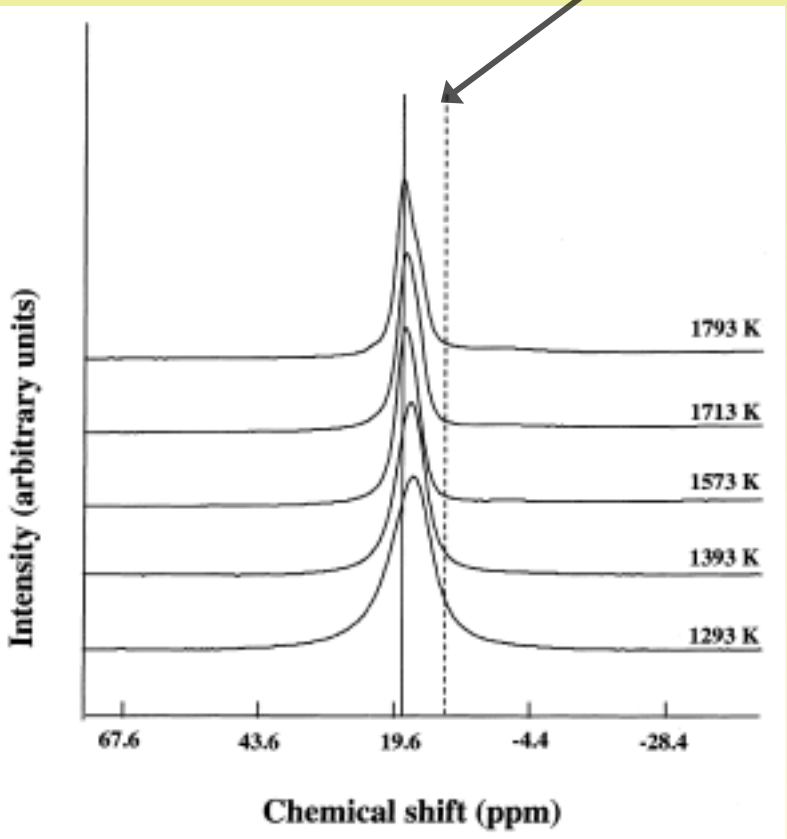


No shift of the B-O peak up to Tg

Coordination change onset above Tg

High-temperature NMR results

Sen, J. Non-Cryst. Solids, 253(1999)84



Na diborate

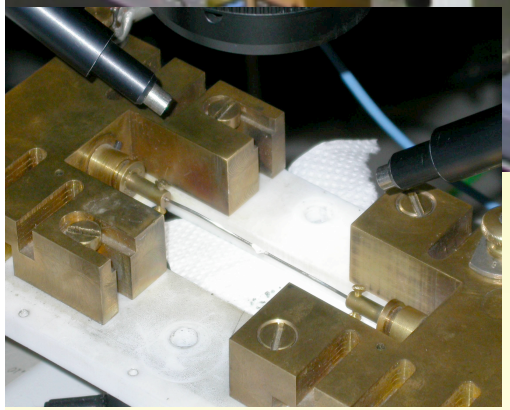
Position if no change

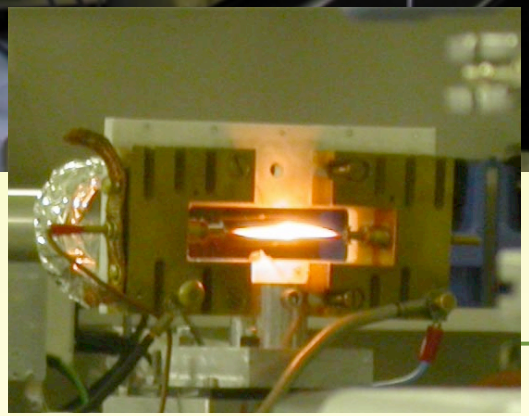
NMR shows a boron coordination change

but averaging of the two chemical shifts

⇒ quantification difficult

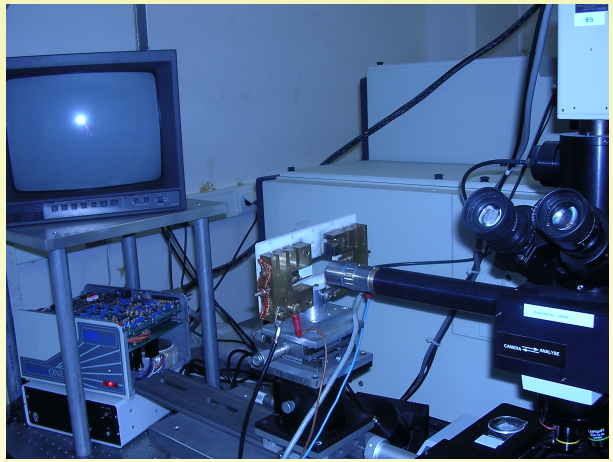
High temperature Raman spectroscopy



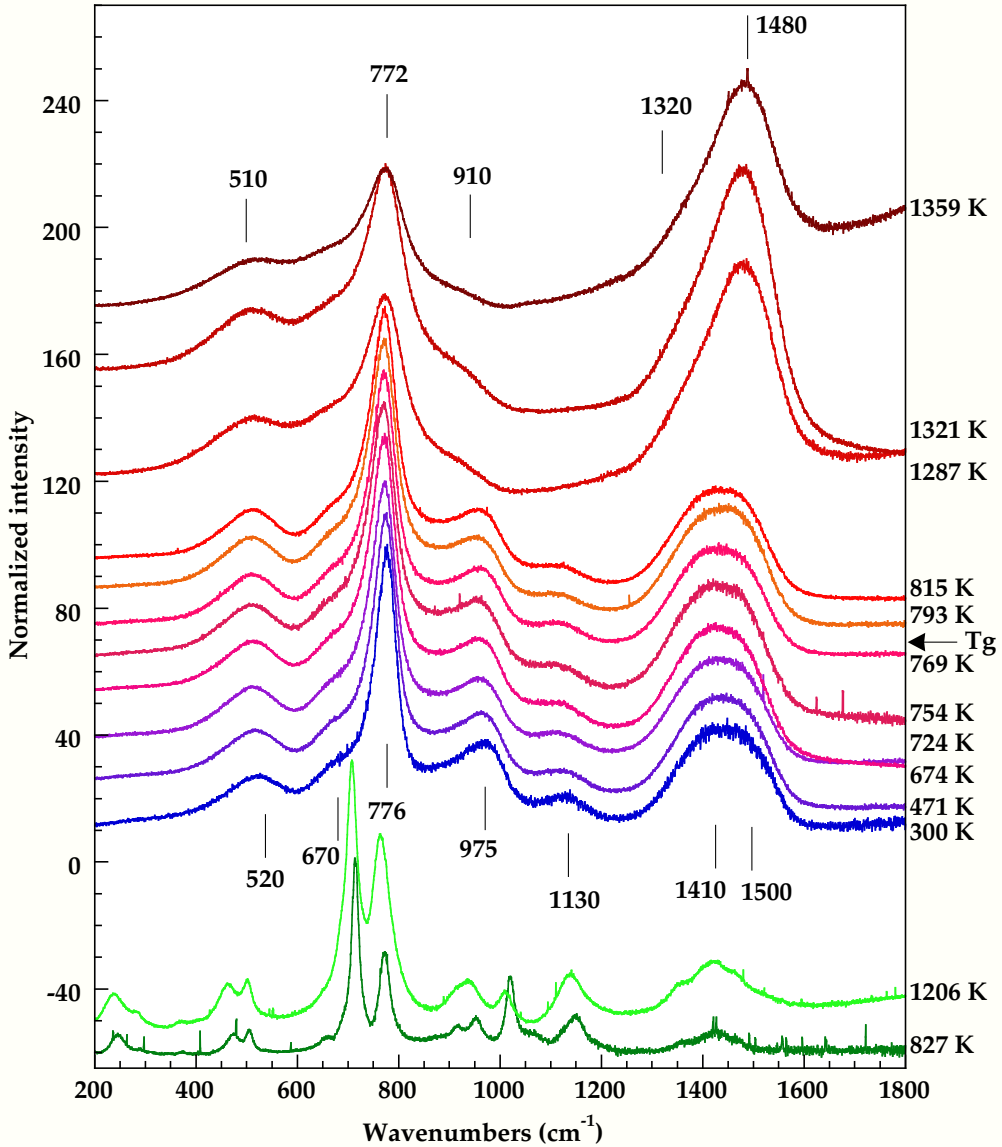


Jobin Yvon T 64000
λ=514 nm Ar^+ laser
CCD detector

Furnace: Pt wire with a hole



High temperature Raman spectra for LB2



Cormier et al., J. Am. Ceram. Soc., 89(2006)13

In the glass:

- Medium frequency bands:

borate groups containing BO_4 tetrahedra (mainly diborate and tetraborate)

- High frequency bands:

due to B-O and B-NBO stretching
band at 1410 cm^{-1} related to BO_4
band at 1500 cm^{-1} related to BO_3

In the liquid:

- Medium frequency bands:

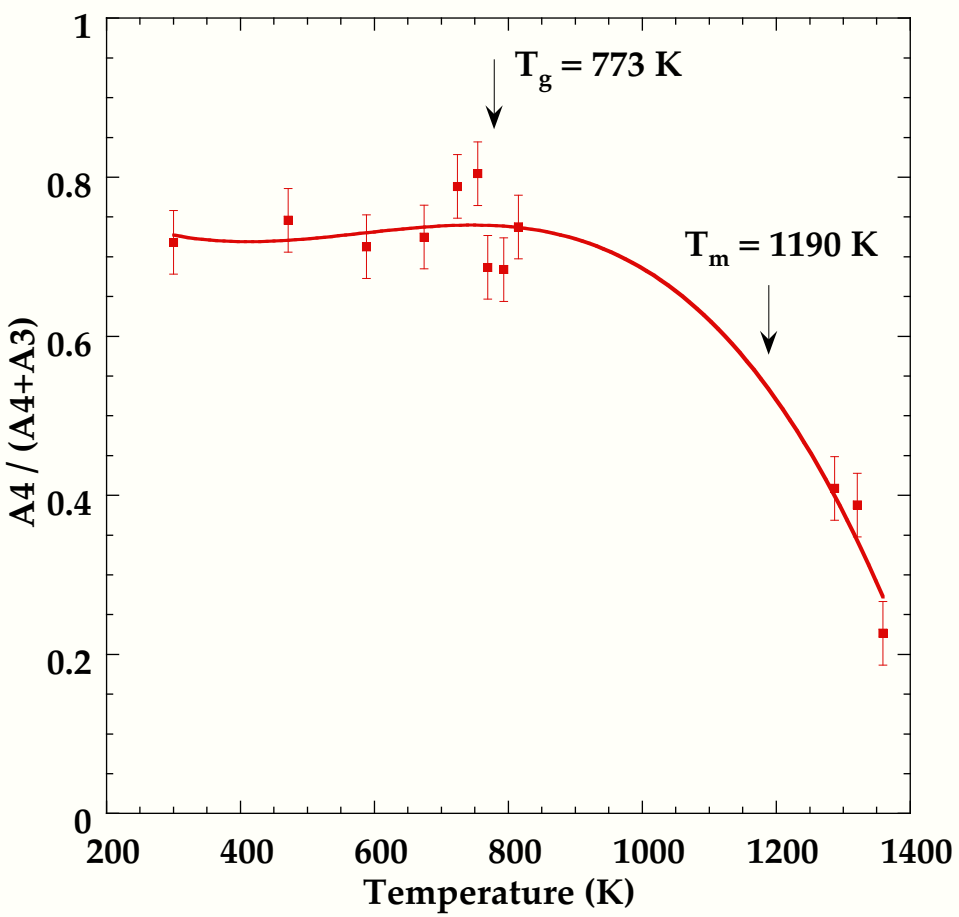
disappearance of the borate groups

- High frequency bands:

change in relative intensity of the two bands

⇨ Agree with less BO_4 in the liquid and more NBOs

Proportion of BO_4 determined by Raman



Area ratio of the two high frequency bands (Gaussian fit)

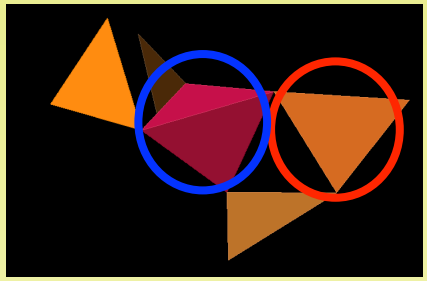
- Important decrease of the low frequency band associated with BO_4 tetrahedra
- Conversion begins only above Tg
- Indirect evaluation

Détermination qualitative de la coordinence du bore en température

- **Calibration avec une technique quantitative (RMN et neutrons)**

K diborate: Akagi et al., J. Non-Cryst. Solids, 293-295 (2001) 471
Na diborate: Yano et al., J. Non-Cryst. Solids 321 (2003) 137

High temperature Raman spectra for xNa_2O-$(1-x)B_2O_3$



2 boron-site geometry :

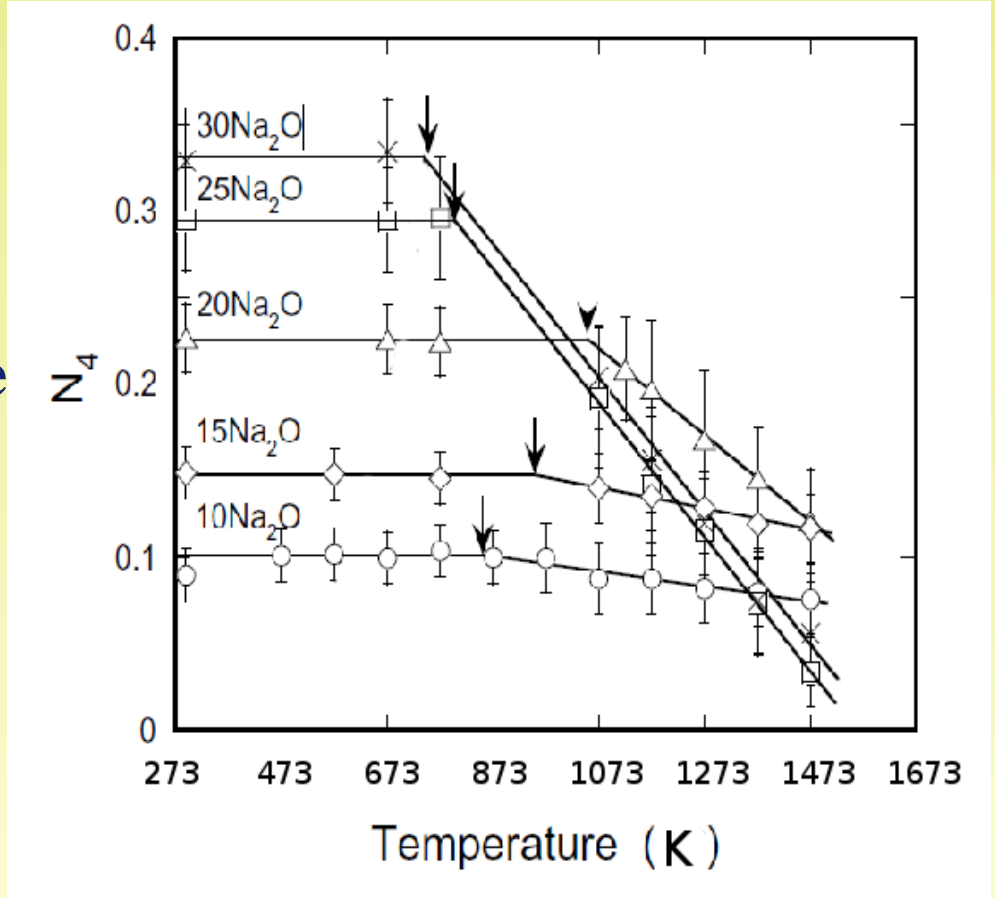
BO_4 tetrahedron BO_3 triangle

With increasing temperature :

$$^{[4]}B \rightarrow {}^{[3]}B + NBO$$

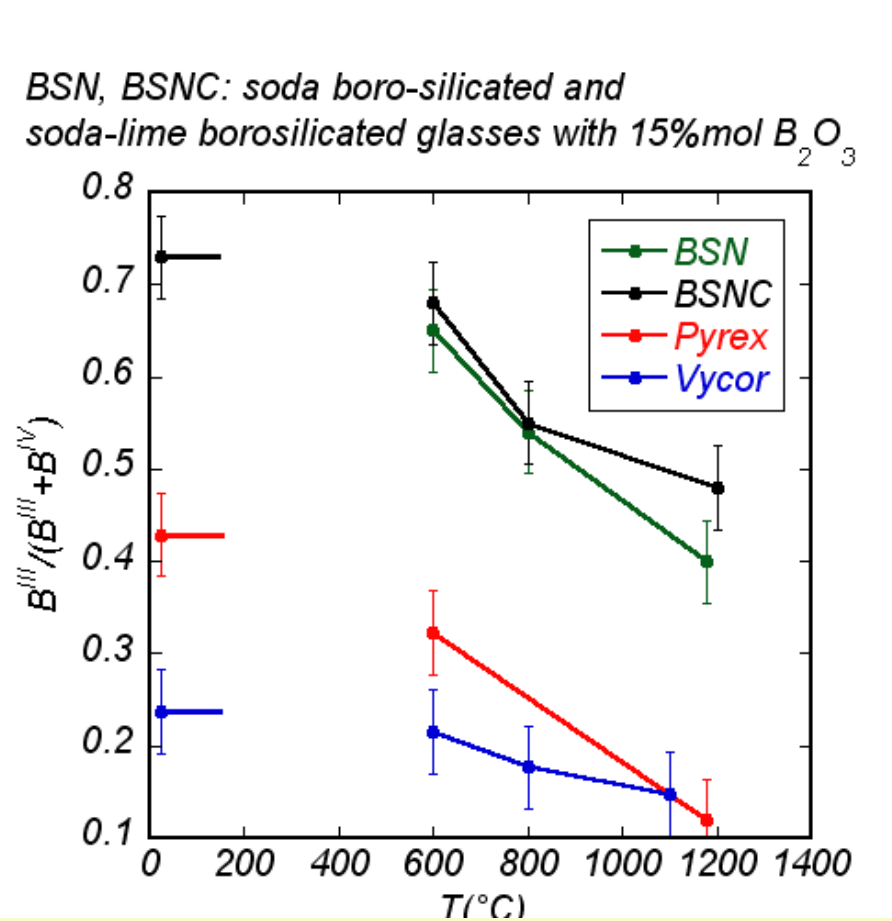
$$N_4 = \frac{^{[4]}B}{^{[4]}B + {}^{[3]}B}$$

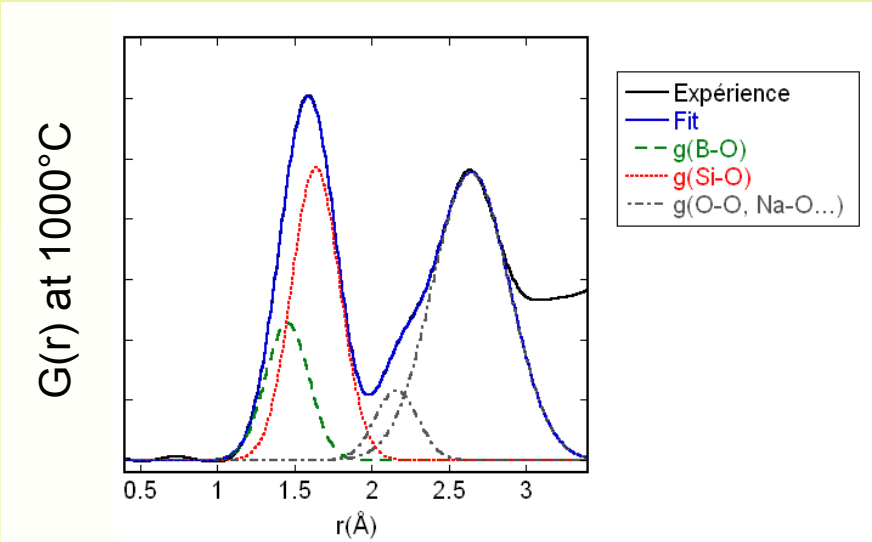
Raman, in situ study of an alkali borate



Yano et al. J. Non-Cryst. Solids 321(2003)147

BO_4 to BO_3 conversion in borosilicates



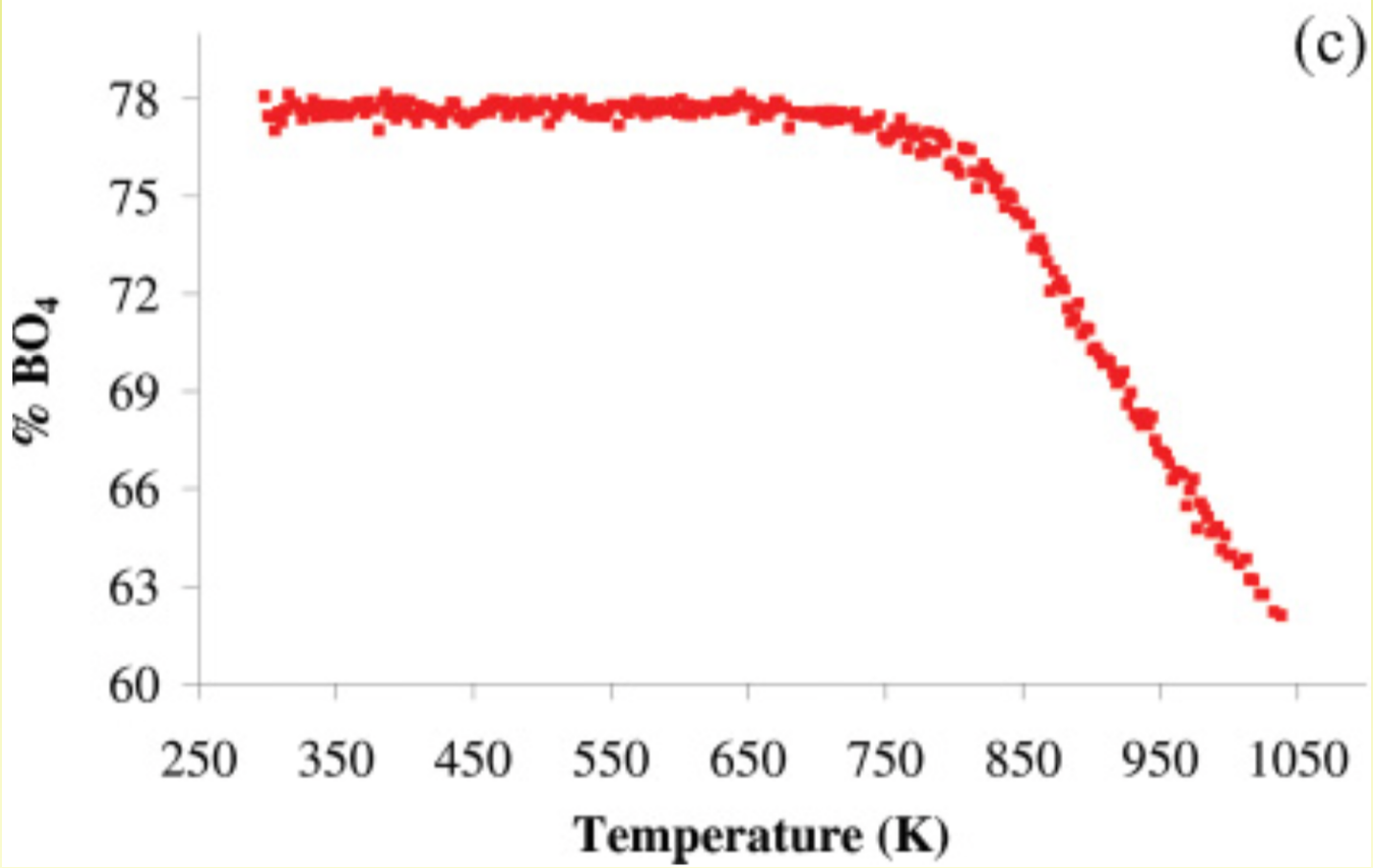


Michel et al. J. Non-Cryst. Solids 379(2013)169

Main results:

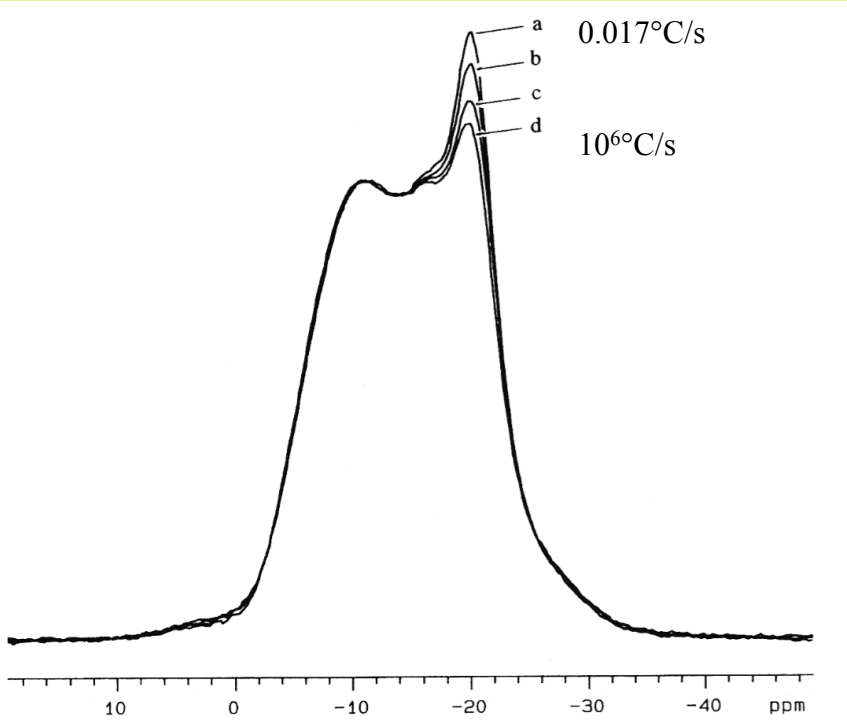
- Initial coordination follows the Dell and Bray model
- Systematic drop of BO_3 with temperature

BO_4 to BO_3 conversion in borosilicates



Angeli et al., Physical Review B, 85(2012)54110

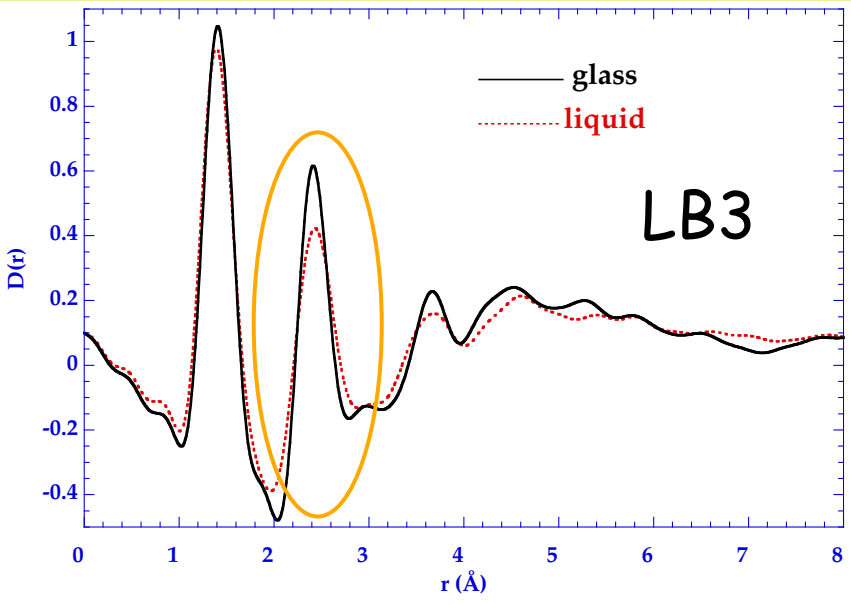
Effect of fictive temperature

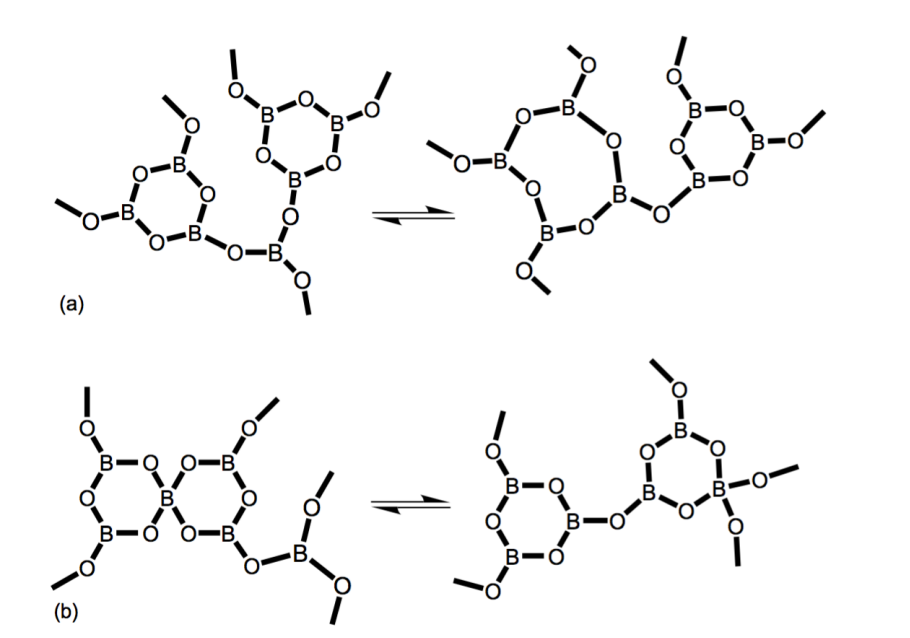


Fraction of BO_4 decreases as the fictive temperature increases

Sen & Ellsworth, J. Am. Ceram. Soc. 79(1996)2247

Changes at intermediate range





- Broadening of the B-B peak:
- Opening of the network due to more NBO and disappearance of rings, in agreement with Raman:

Cormier et al., J. Am. Ceram. Soc., 89(2006)13

Environment of alkalis ?

Less BO_4, more NBO ⇒ Consequences for the alkalis ?

Study of the environment around Li using neutron diffraction coupled with isotopic substitution technique:

Principle: canceling contributions from the borate network

$$S_6(Q) = \sum_{\substack{\alpha\beta \\ \alpha \neq Li}} c_\alpha c_\beta b_\alpha b_\beta (S_{\alpha\beta}(Q) - 1) + \sum_{\alpha Li} c_\alpha c_{Li} b_\alpha b_{Li}^6 (S_{\alpha Li}(Q) - 1)$$

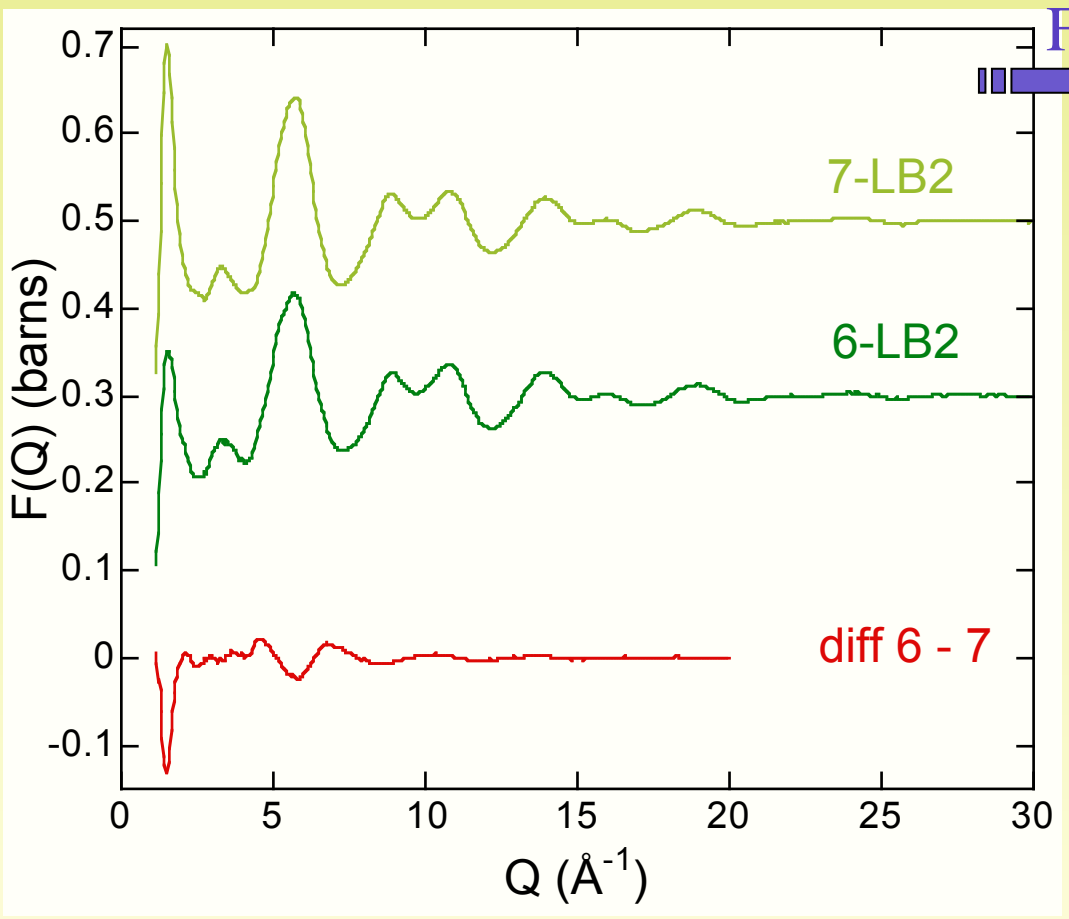
$$S_7(Q) = \sum_{\substack{\alpha\beta \\ \alpha \neq Li}} c_\alpha c_\beta b_\alpha b_\beta (S_{\alpha\beta}(Q) - 1) + \sum_{\alpha Li} c_\alpha c_{Li} b_\alpha b_{Li}^7 (S_{\alpha Li}(Q) - 1)$$

⇒ We obtain $S_{Li\text{-}\alpha}(Q)$ and $G_{Li\text{-}\alpha}(r)$

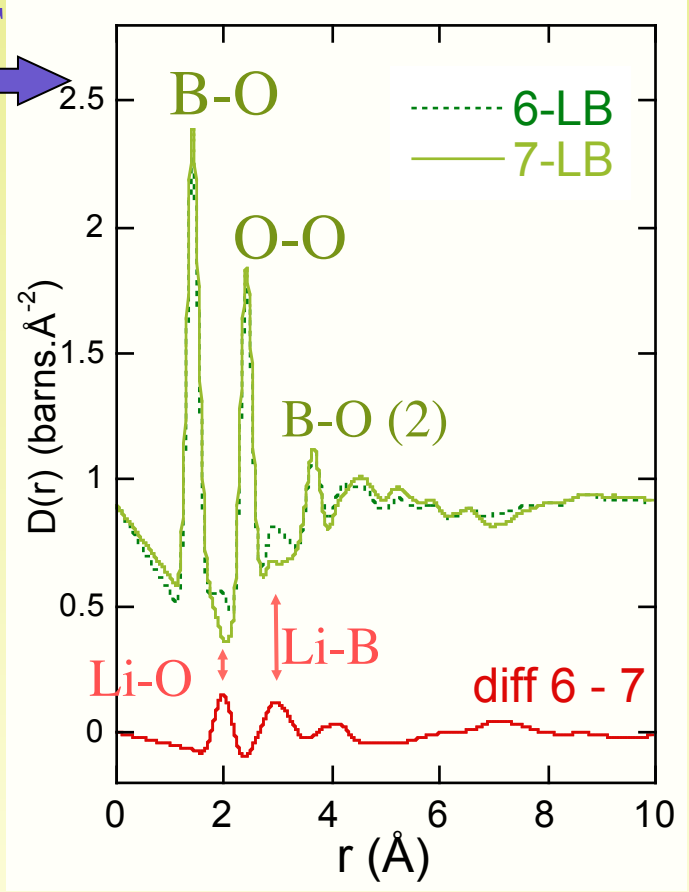
Li site in the glass

Less BO_4, more NBO ➡ Consequences for the alkali ?

$S_{Li-\alpha}(Q)$ et $G_{Li-\alpha}(r)$ obtained by isotopic substitution ofLi

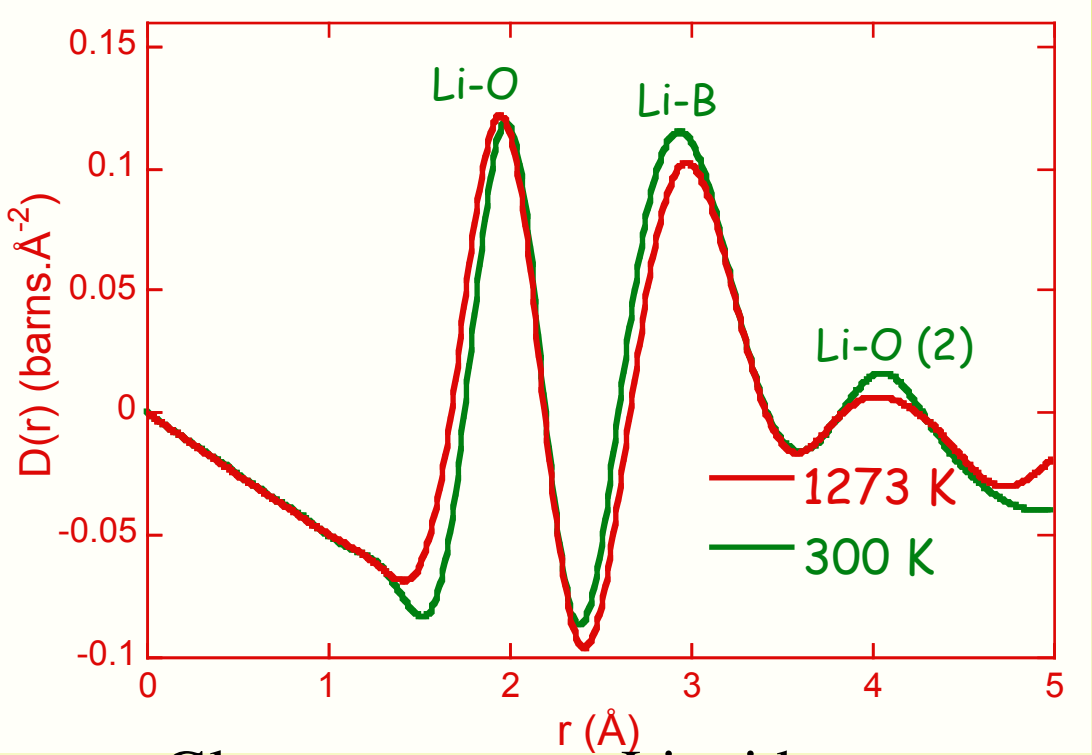


FT



Data obtained on SANDALS at ISIS (UK)

Evolution of the Li site between the glass and the liquid



Data obtained on 7C2 at LLB (France)

Shortening of the mean Li-O distance by -0.02Å

dLi-NBO < dLi-BO

Higher number of NBO in the first coordination sphere of Li in liquids

Glass → Liquid

MOn → (MOn')'

M compensator → M modifier

⇨ Modifications of the Li environment associated with a change of its structural role in the liquid

Majérus et al. J. Phys. Chem. B 107 (2003) 13044

Evolution of the Li site between the glass and the liquid

Glass → Liquid

$B\varnothing_4^- + MO_n \longrightarrow B\varnothing_3 + NBO^- + (MO_{n'})'$

M compensator — M modifier

⇒ Modifications of the Li environment associated with a change of its structural role in the liquid

Equilibrium of the BO_4/BO_3 conversion in the liquid

$$B\varnothing_4^- + MO_n \longrightarrow B\varnothing_3 + NBO + (MO_{n'})'$$

M compensator — M modifier

Equilibrium constant at temperature *i*

$$K_i = C \times \frac{X^i_{BO_3}\, X^i_{NBO}}{X^i_{BO_4}}$$

$$X_{BO_4} = N4$$

$$X_{BO_3} = 1 - N4$$

$$X_{NBO} = R - N4$$

C : rapport des coefficients d'activités de chaque espèce, constant avec T

Equilibrium of the BO_4/BO_3 conversion in the liquid

$$B\varnothing_4^- + MO_n \longrightarrow B\varnothing_3 + NBO + (MO_{n'})'$$

M compensator — M modifier

$$K_i = C \times \frac{X^i_{BO_3}\, X^i_{NBO}}{X^i_{BO_4}}$$

$$X_{BO_4} = N4$$

$$X_{BO_3} = 1 - N4$$

$$X_{NBO} = R - N4$$

Van't Hoff's relation : variation of the equilibrium constant with T and the standard enthalpy difference

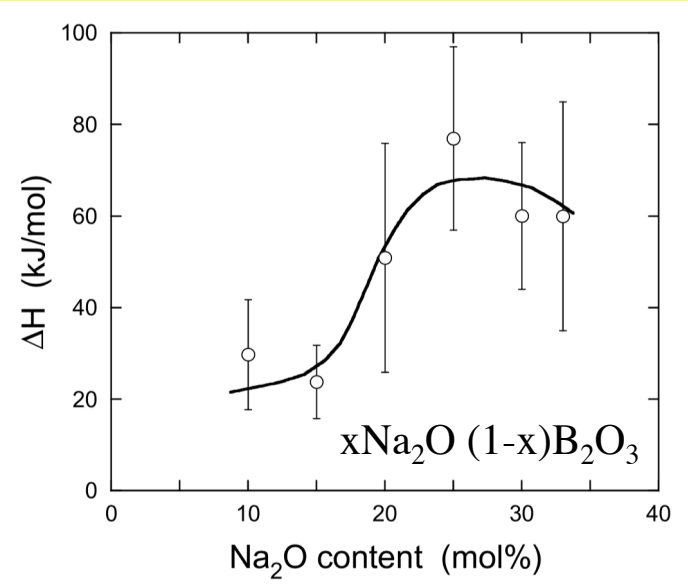
$$\frac{\partial \ln K}{\partial T} = \frac{\partial\left(-\Delta G^0 / RT\right)}{\partial T} = \frac{\Delta H^0}{RT^2}$$

Equilibrium of the BO_4/BO_3 conversion in the liquid

Between $T_1=T_g$ and $T_2=T_{liquid}$

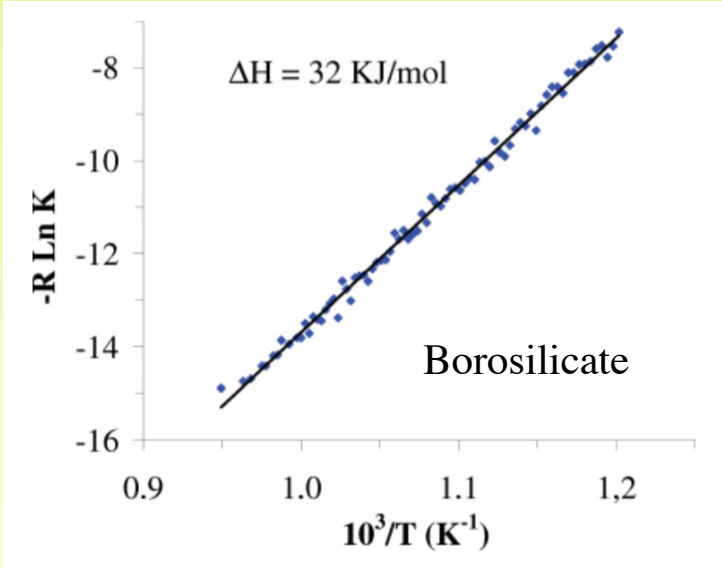
$$\Delta H^0 = -R\frac{\ln K_1 - \ln K_2}{\frac{1}{T_1} - \frac{1}{T_2}}$$

ΔH per mole of B ≡ enthalpy difference if one mole BO_4 converted completely to one mole BO_3



Yano et al. J. Non-Cryst. Solids 321(2003)147

Borosilicate



Angeli et al., Physical Review B, 85(2012)54110

Equilibrium of the BO_4/BO_3 conversion in the liquid

$$B\varnothing_4^- + MO_n \longrightarrow B\varnothing_3 + NBO + (MO_{n'})'$$

M compensator — M modifier

Cp related to the configuration entropy can be estimated

$$Cp = \frac{\Delta H \Delta X}{T_1 - T_2} \qquad \text{(J/mol/K)}$$

ΔX : number of moles of B converted per mole of glass

Configuration entropy related to structural changes above Tg

⇒ Contribution to the configurational properties ?

B_2O_3: no coordination change => strong liquid

√ Boron coordination change

Glass → Liquid

BO_4^- → BO_3 + NBO^-

Alkali borate

ΔH=12-37 kJ mol^{-1}

ΔCp of the reaction (loi de Van't Hoff)

$\Delta C_p \approx 16\ J.mol^{-1}.K^{-1}$ $(\Delta C_p^{conf} = 71\ J.mol^{-1}.K^{-1})$

Cormier et al., J. Am. Ceram. Soc. 89(2006)13 *Uhlmann et al., J. Non-Cryst. Solids, 5(1971)426*

Borosilicate

ΔH=32 kJ mol^{-1}

ΔCp of the reaction (loi de Van't Hoff)

$\Delta C_p \approx 2.1\ J.mol^{-1}.K^{-1}$ $(\Delta C_p^{conf} = 8.6\ J.mol^{-1}.K^{-1})$

Angeli et al., Physical Review B, 85(2012)54110

Configuration entropy related to structural changes above Tg

⇒ Contribution to the configurational properties ?

√ Boroxol ring rupture (*Walrafen et al., J. Chem. Phys., 79(1983)3609*)

$\Delta H = 27$ kJ mol^{-1}

Both local and medium range changes: two main contributions to the configurational properties but structural changes around Li difficult to estimate