Effect of B_2O_3 addition on the structure and crystallisation properties of soda-lime borosilicate glasses containing lanthanides

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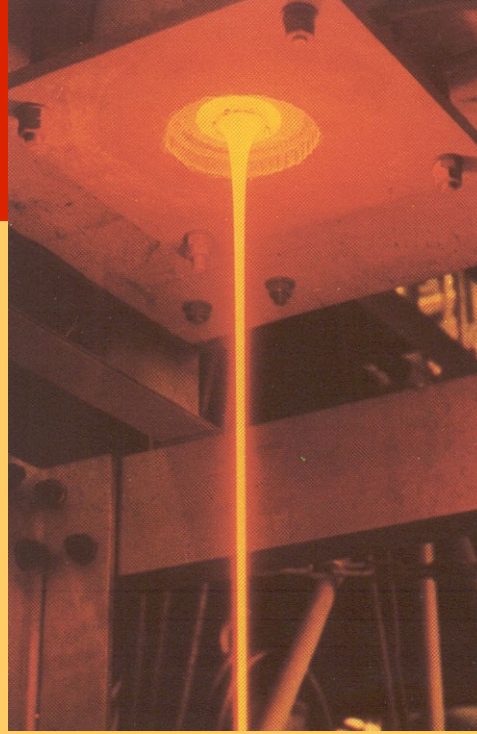
CEA Iramis, SISMM

CEA/DEN/DTCD/SECM/LEDMC

NCM11 – Paris, 2010

Introduction and outline



Context : composition – structure – crystallisation properties relationships in nuclear waste containment glasses

Model glass A (mol %) :

SiO_2	Al_2O_3	B_2O_3	Na_2O	CaO	ZrO_2	RE_2O_3
61.8	3.0	9.0	14.4	6.3	1.9	3.6

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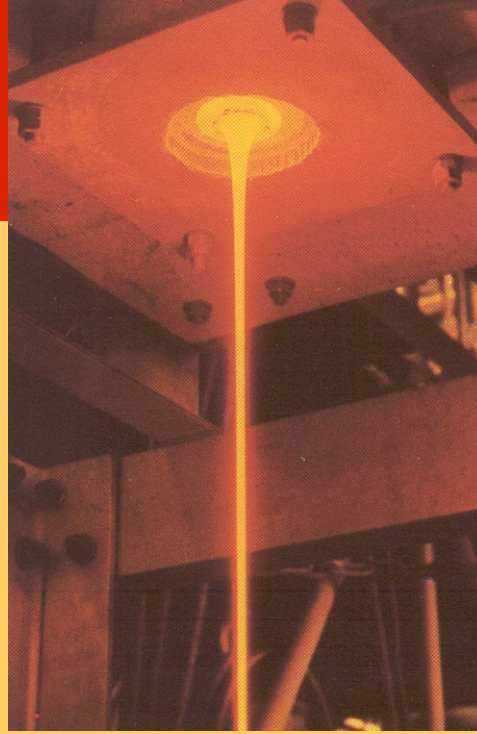

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B_2O_3 is *added* to keep constant all other oxide molar ratios

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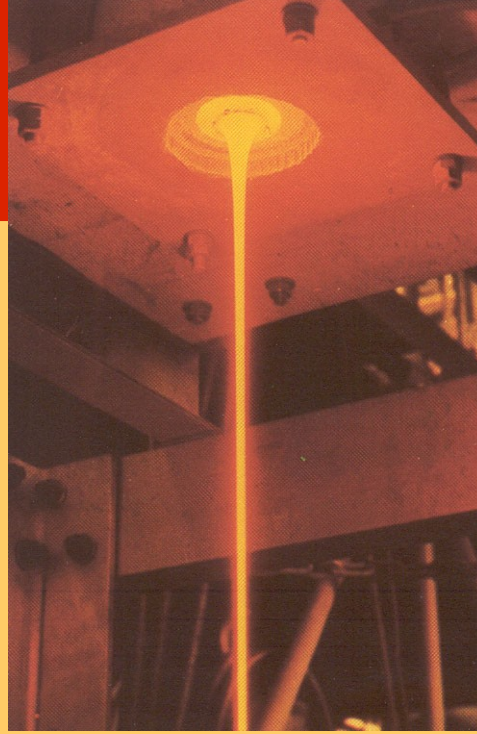

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RE = Nd

Optical absorption, Nd L_3-edge EXAFS

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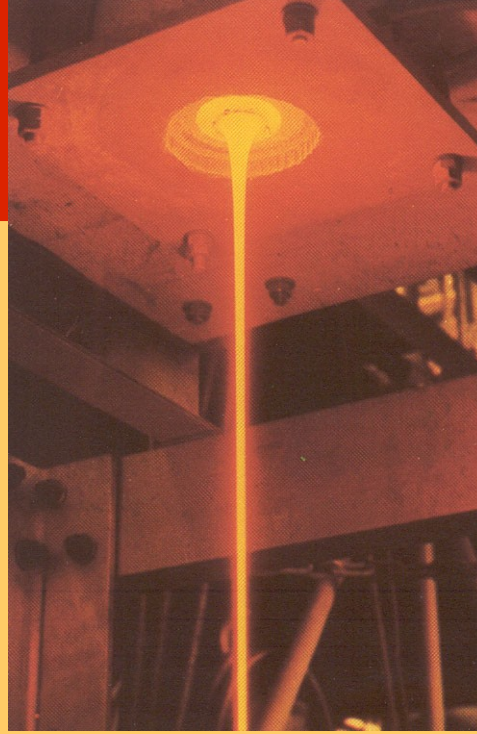

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^{11}B, ^{27}Al, ^{23}Na NMR, Nd^{3+} luminescence

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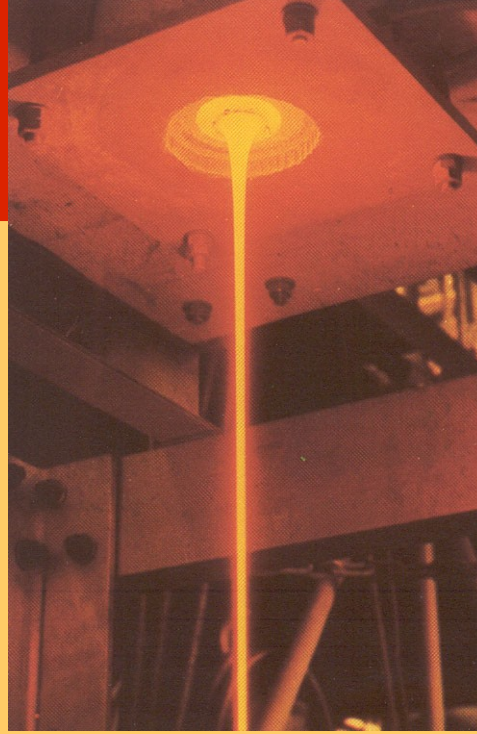

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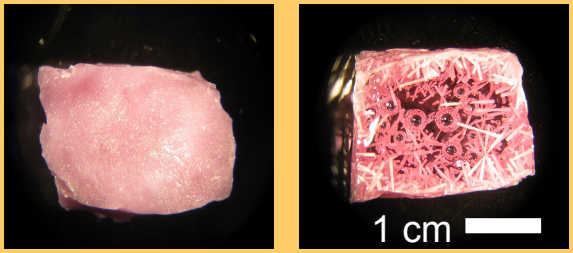
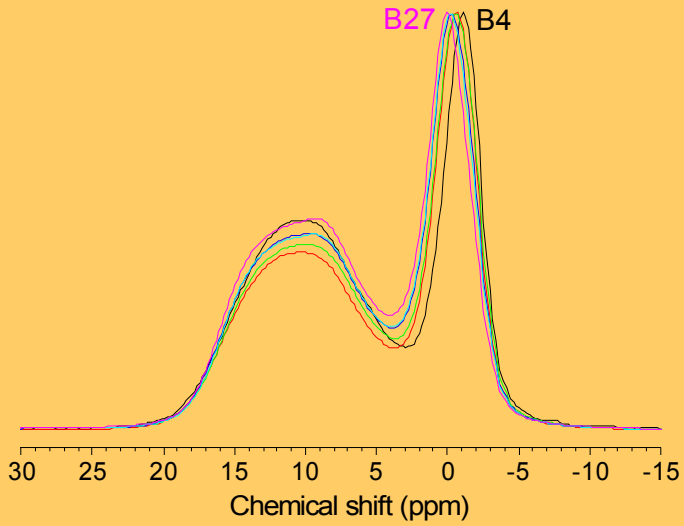


Impact of B_2O_3 content on the crystallisation of a RE-rich silicate phase near $Ca_2Nd_8(SiO_4)_6O_2$ composition

The glass network : ^{11}B and ^{23}Na MAS NMR

^{11}B MAS NMR

N_4 = 40 % accross the Bx series



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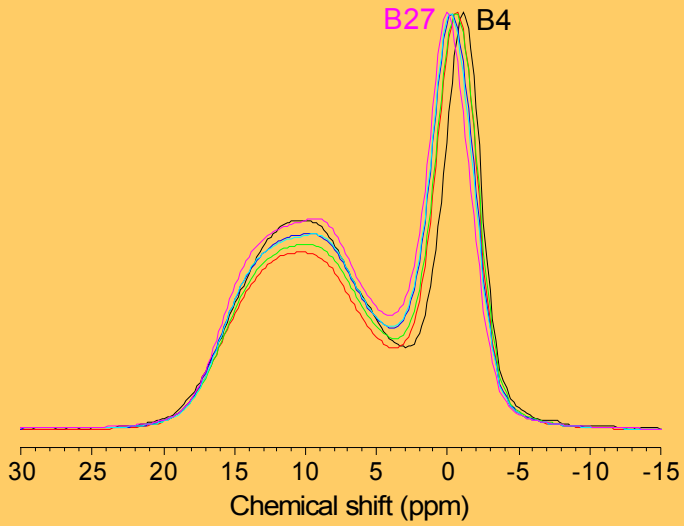

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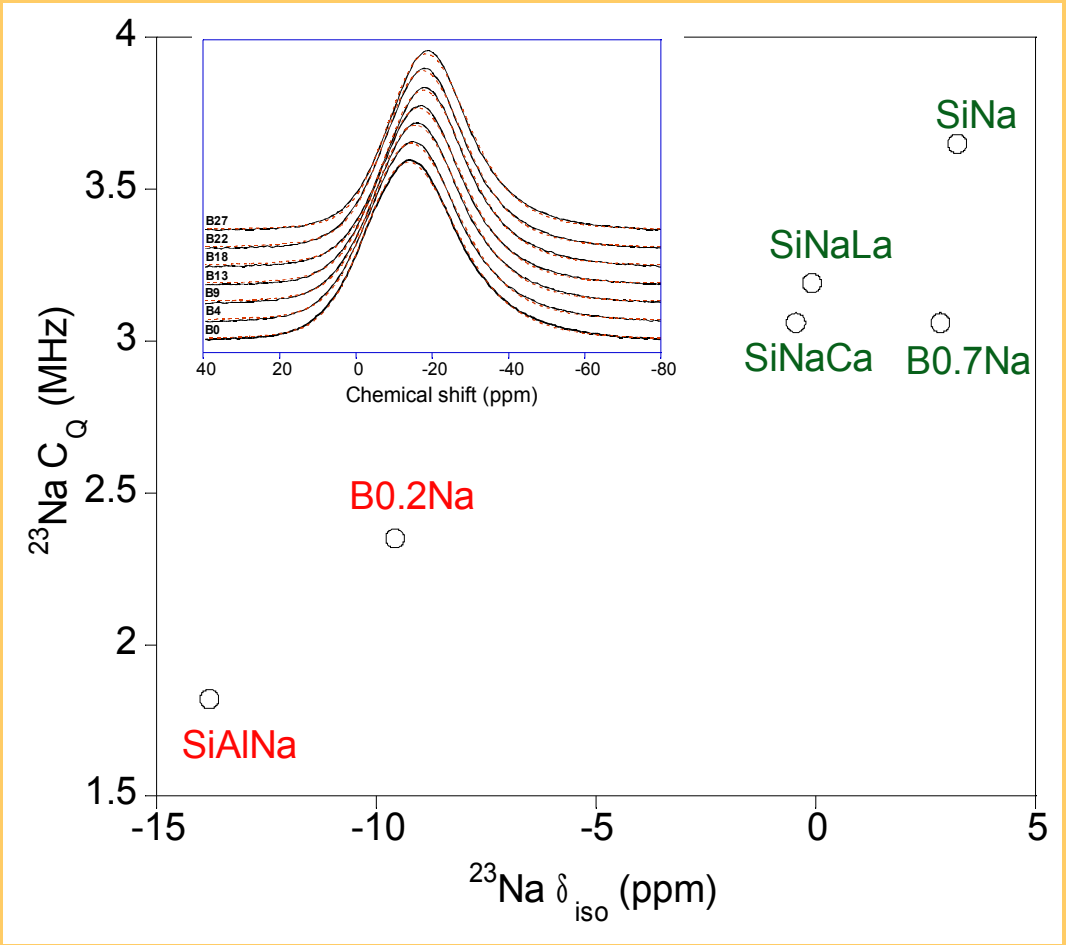

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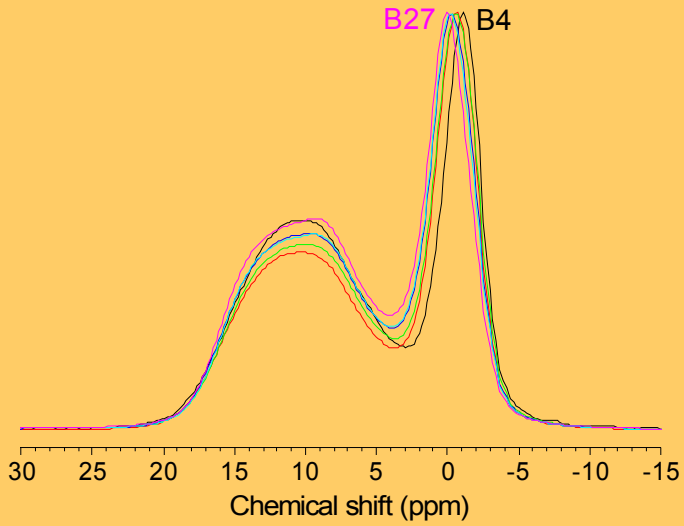

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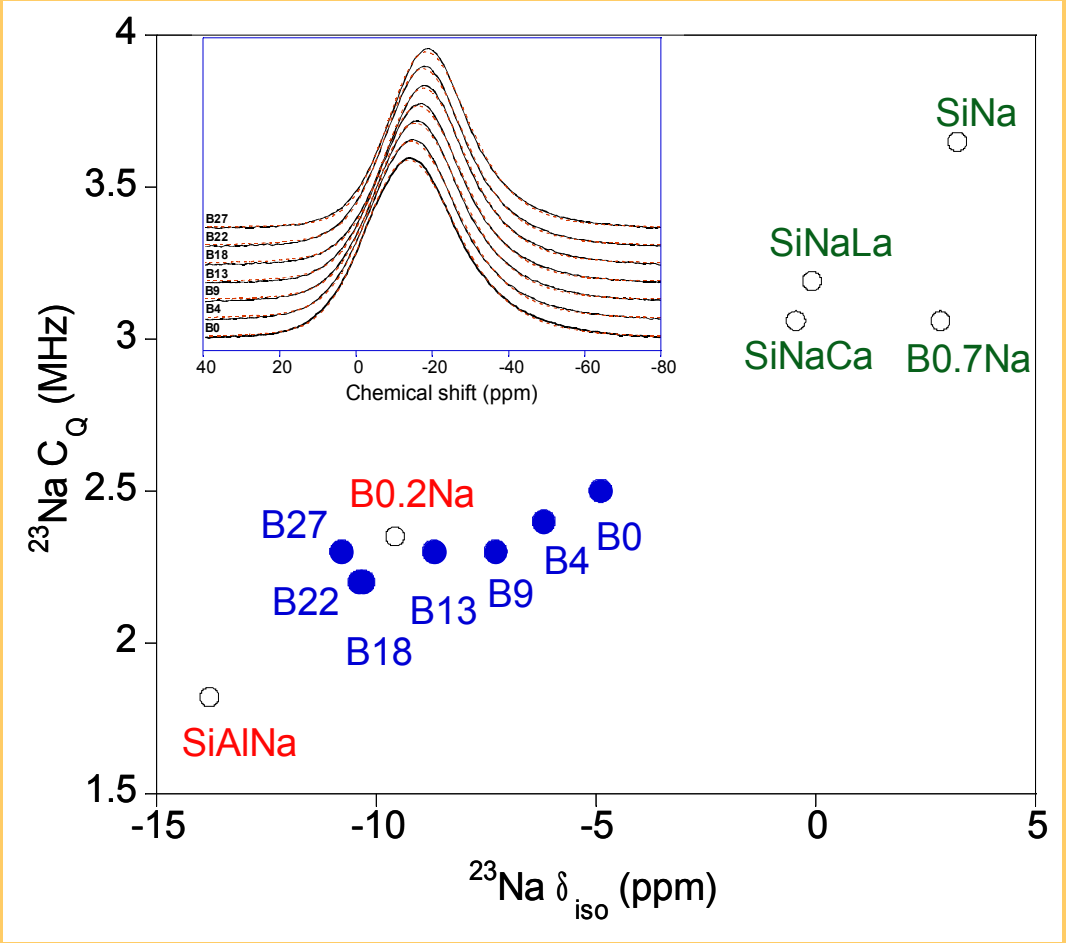

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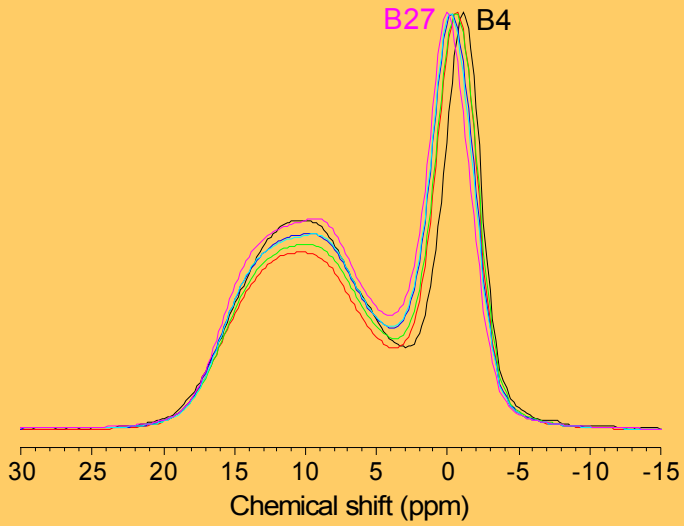

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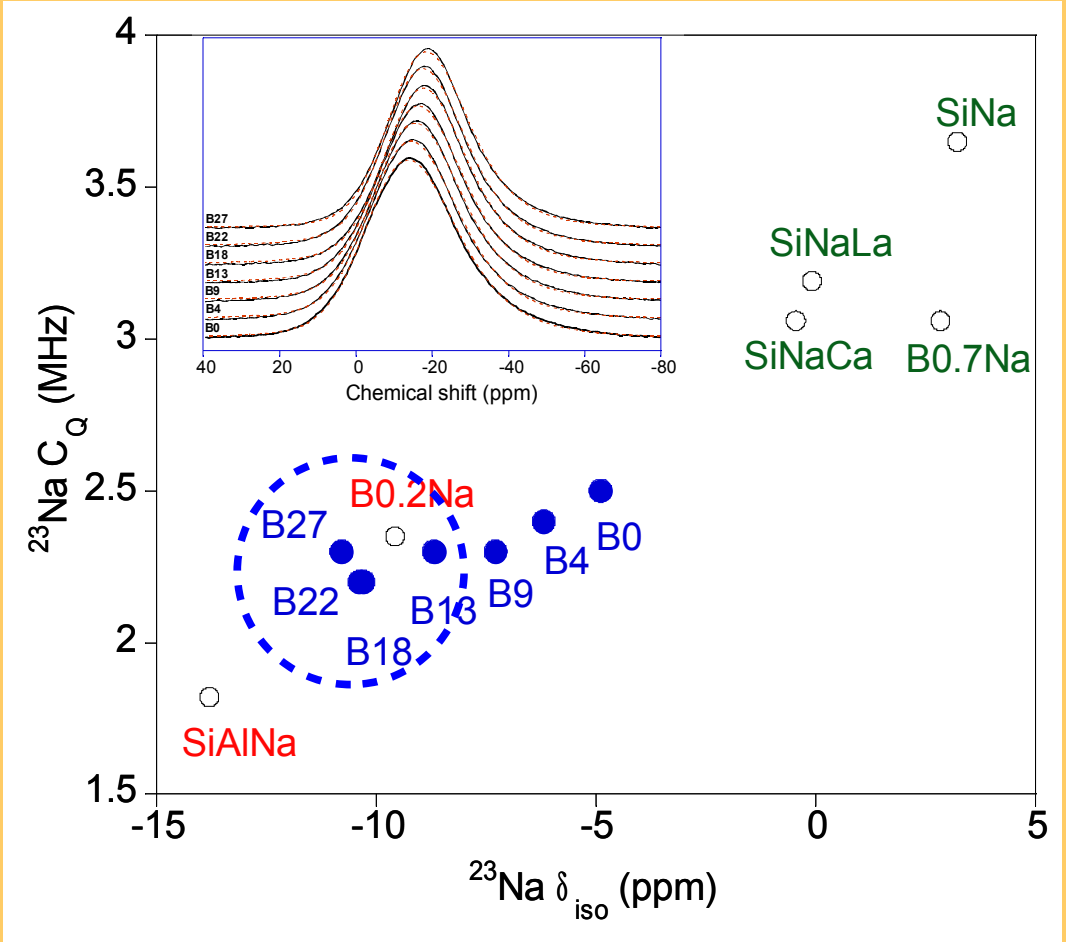
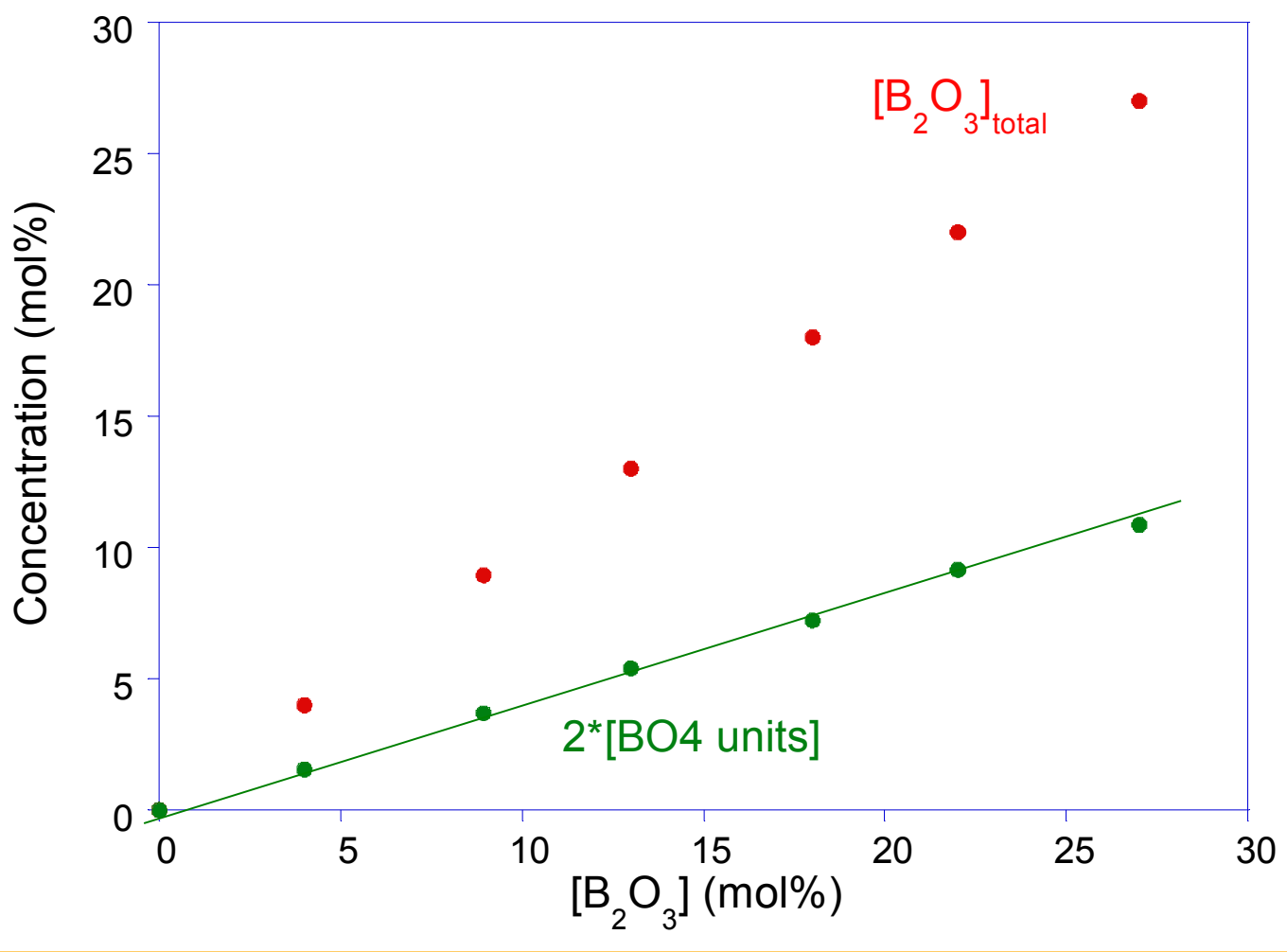


B_2O_3 modifies the structural role of Na^+… and of other cations



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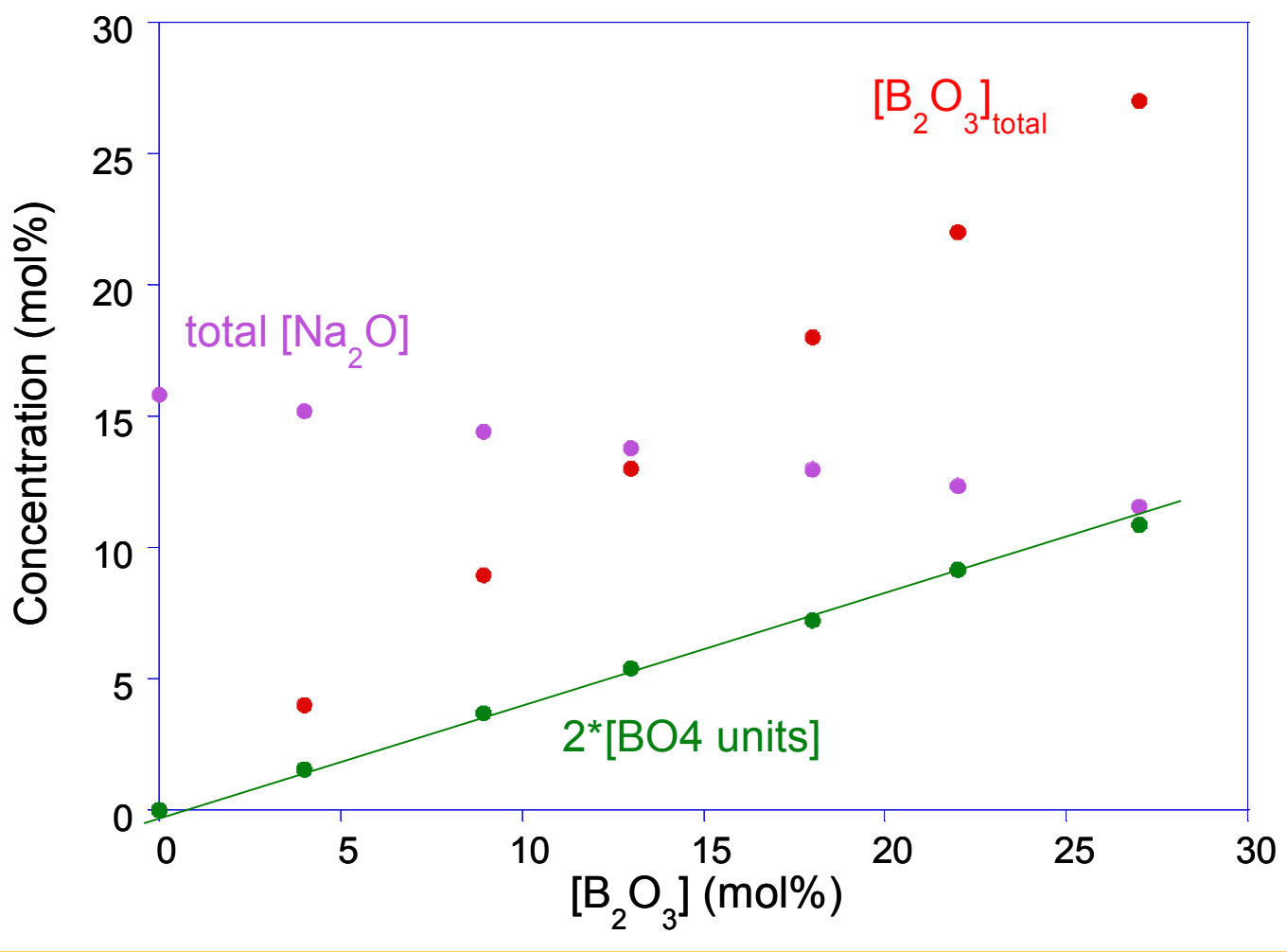

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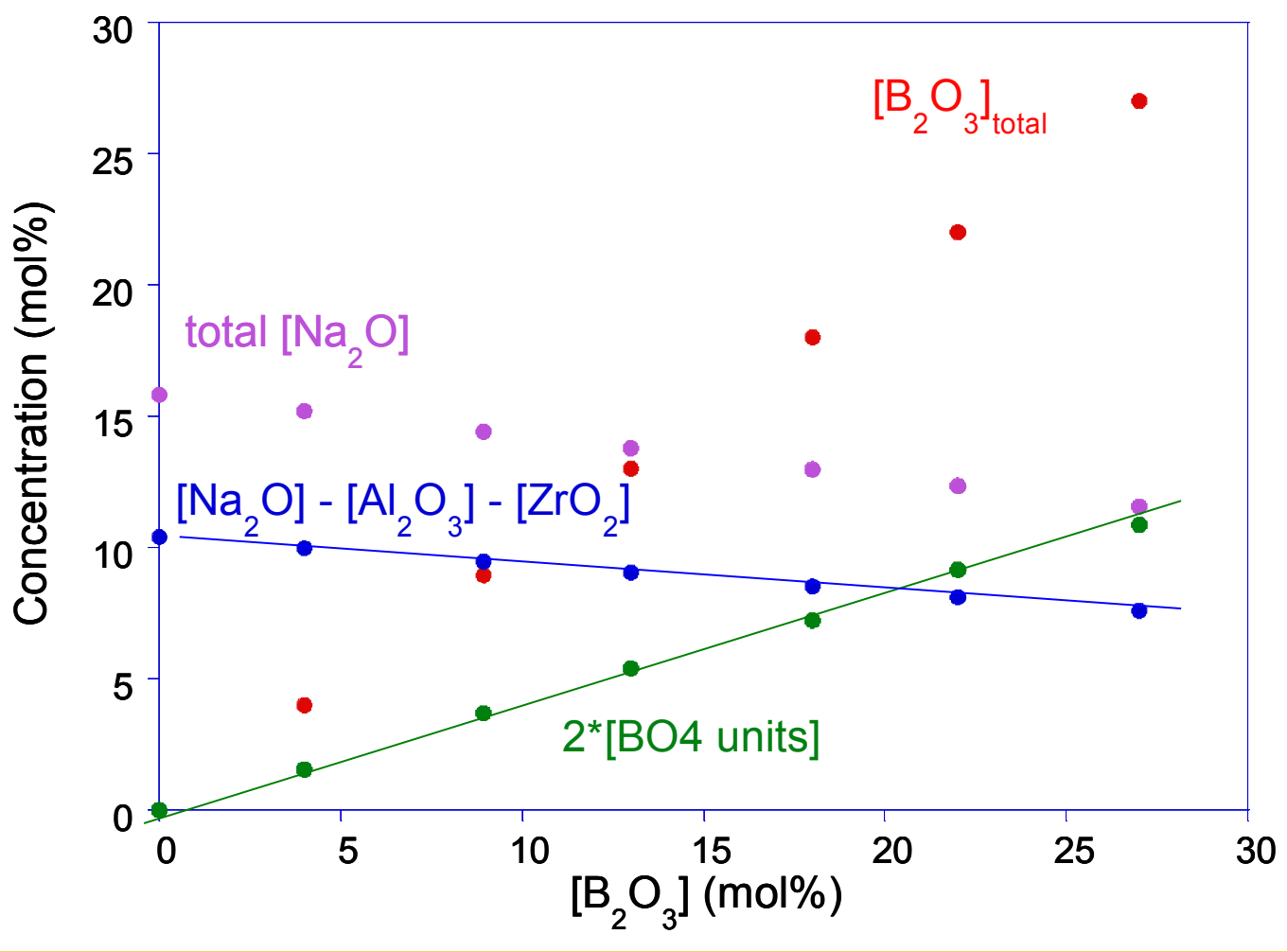

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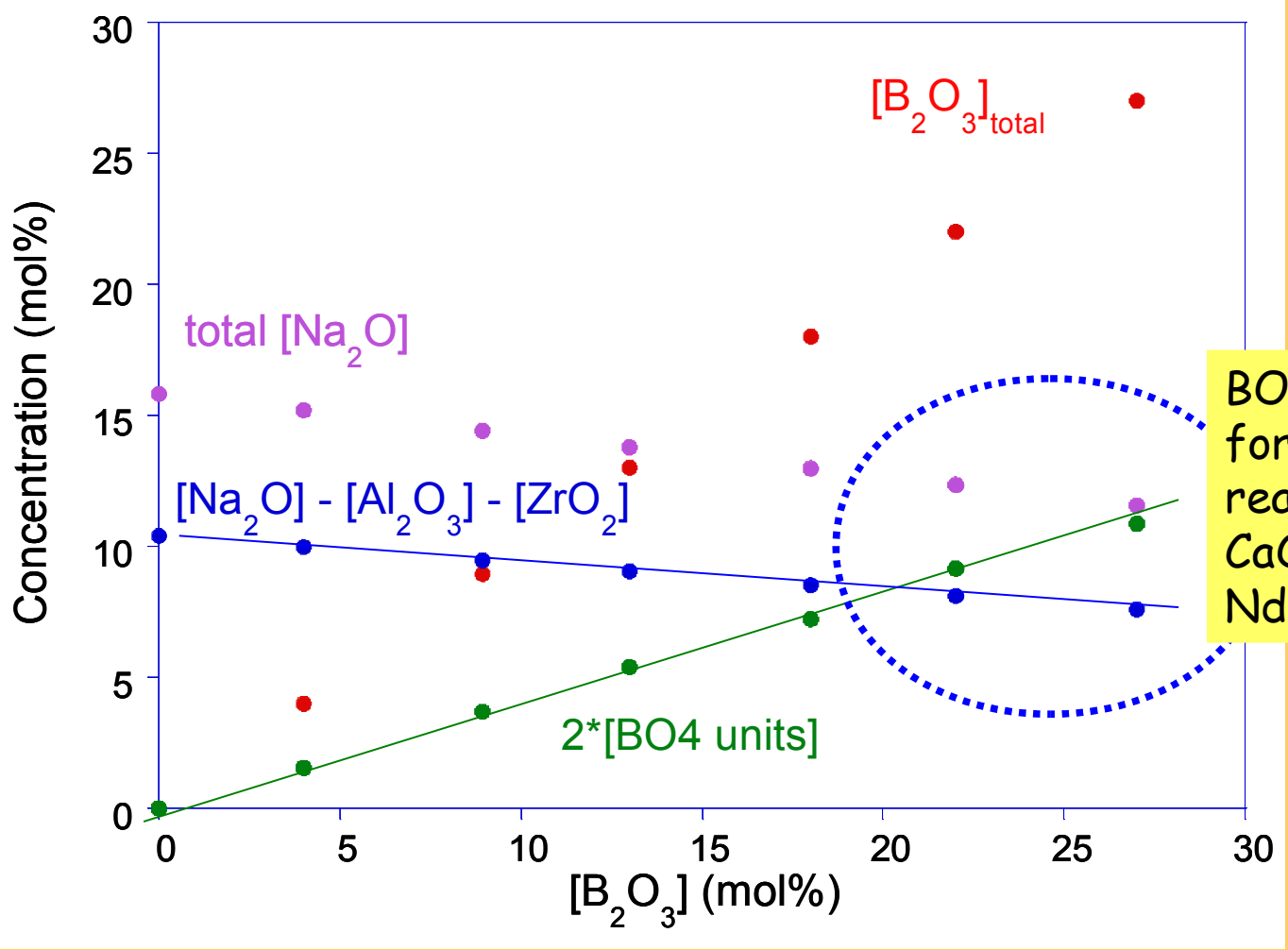
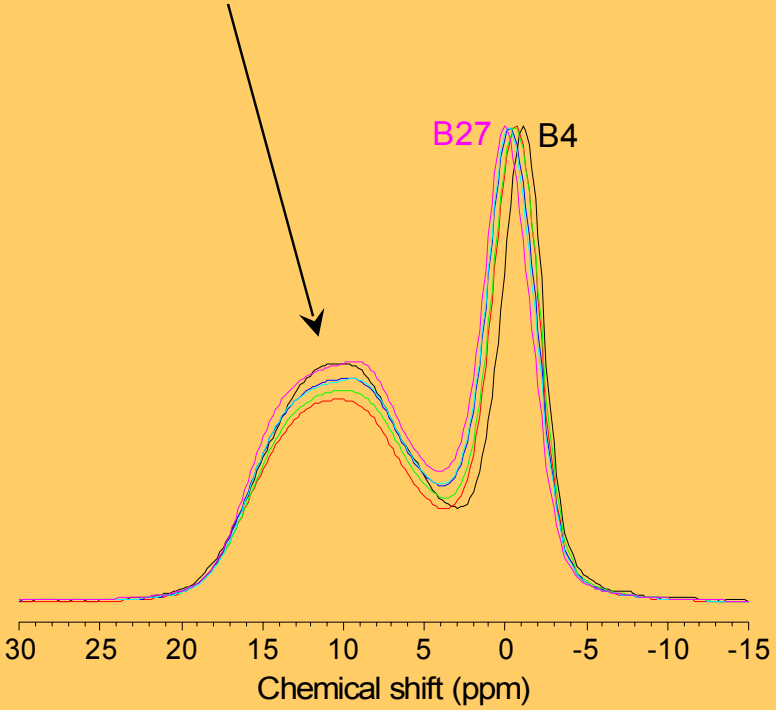


Glass network homogeneity : ^{11}B MAS NMR

Lorentzian broadening because of interaction with Nd^{3+} electronic spin (0.15 mol%) → no valuable fit for BO_3



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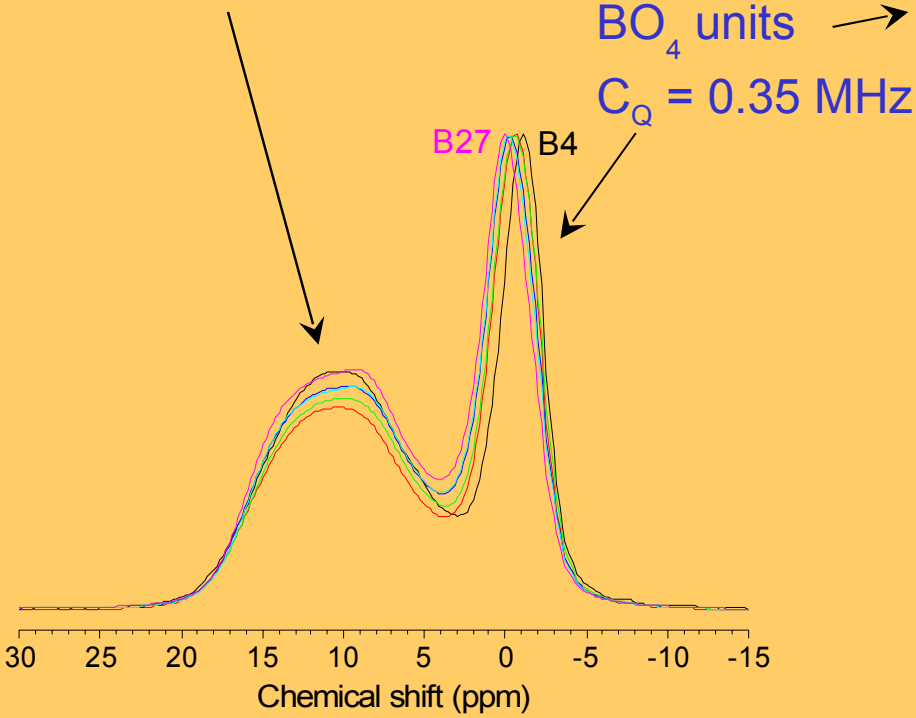

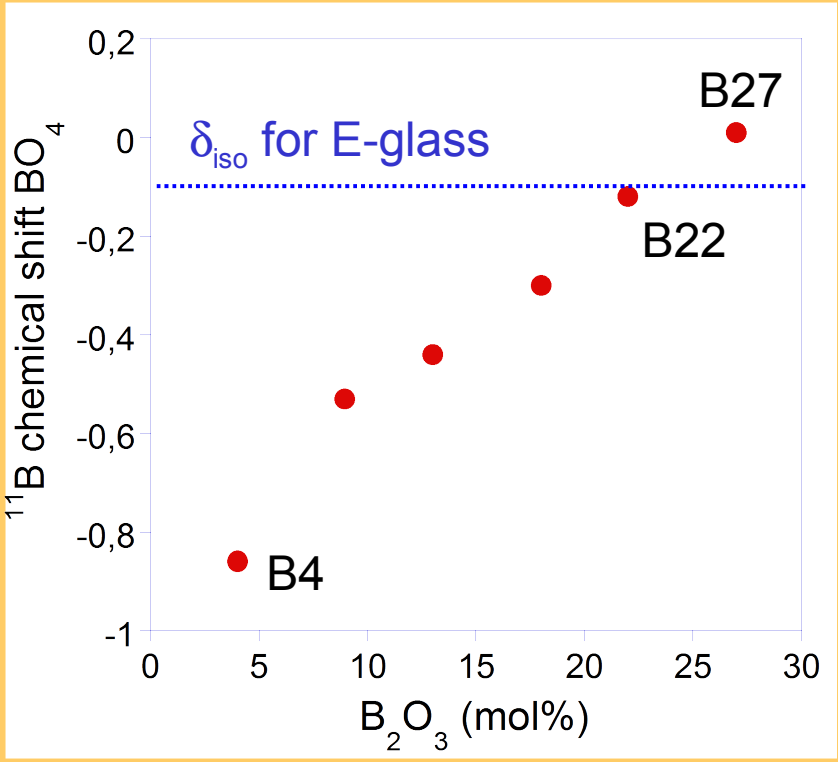

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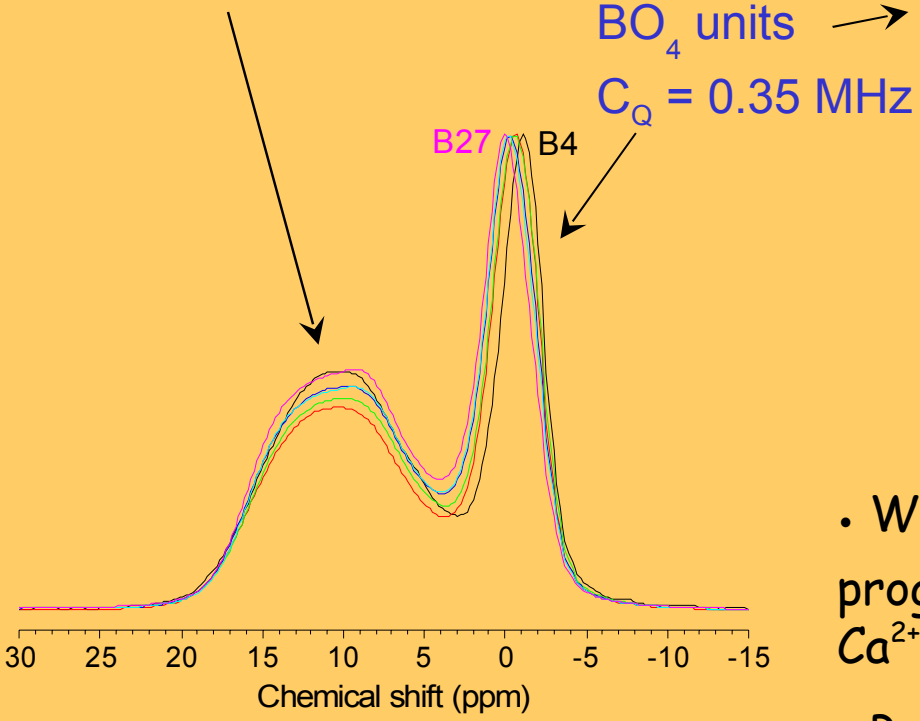
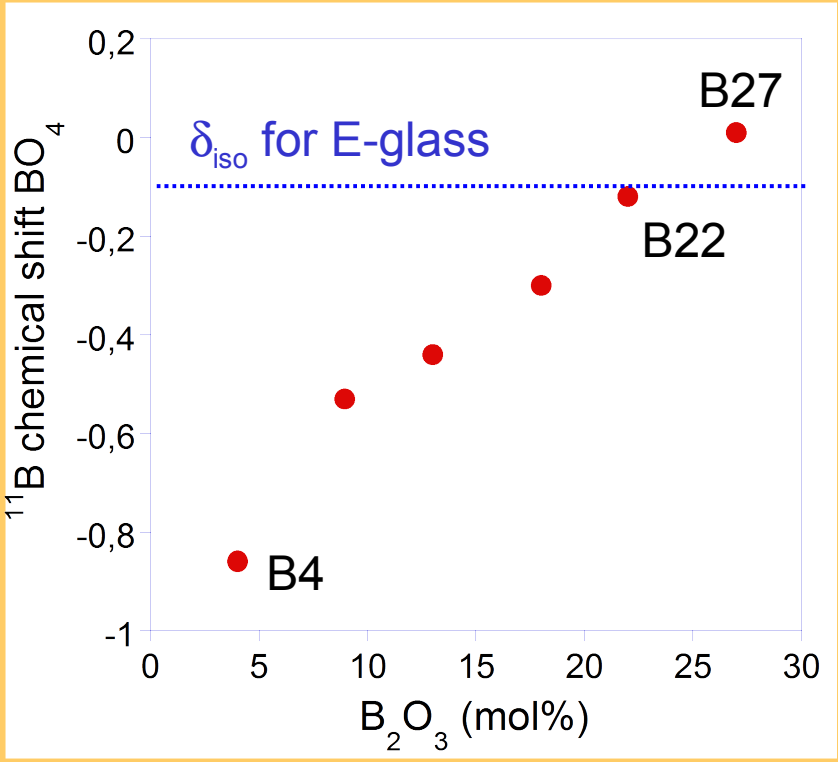
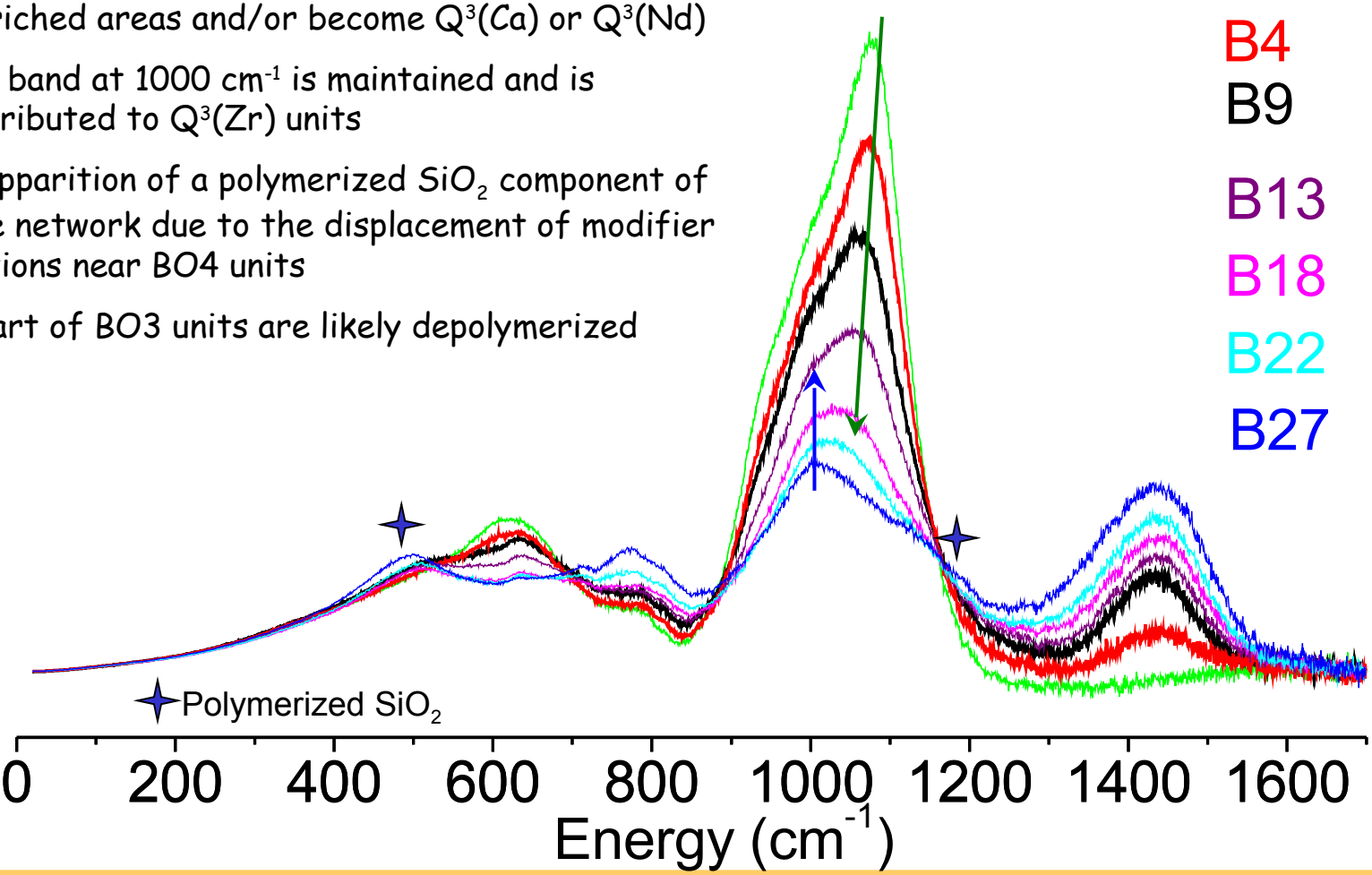




- When adding B_2O_3, new BO4 units are progressively charge-compensated by Ca^{2+} and/or Nd^{3+}
- Progressive B-enrichment around BO_4 units is also possible

Glass network homogeneity : Raman spectroscopy

- Q^3 units decrease in quantity and move toward B-enriched areas and/or become Q^3(Ca) or Q^3(Nd)
- A band at 1000 cm^{-1} is maintained and is attributed to Q^3(Zr) units
- Apparition of a polymerized SiO_2 component of the network due to the displacement of modifier cations near BO4 units
- Part of BO3 units are likely depolymerized



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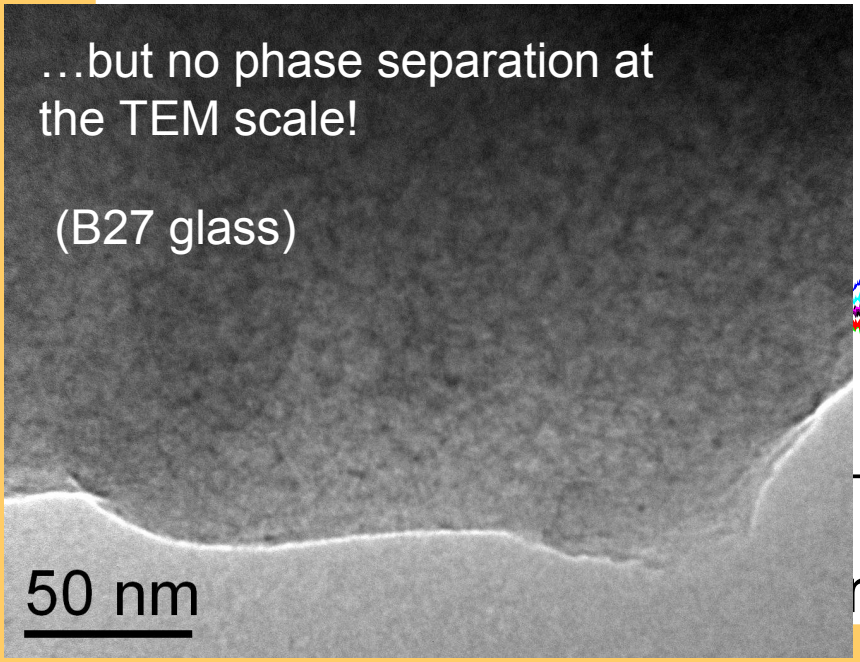
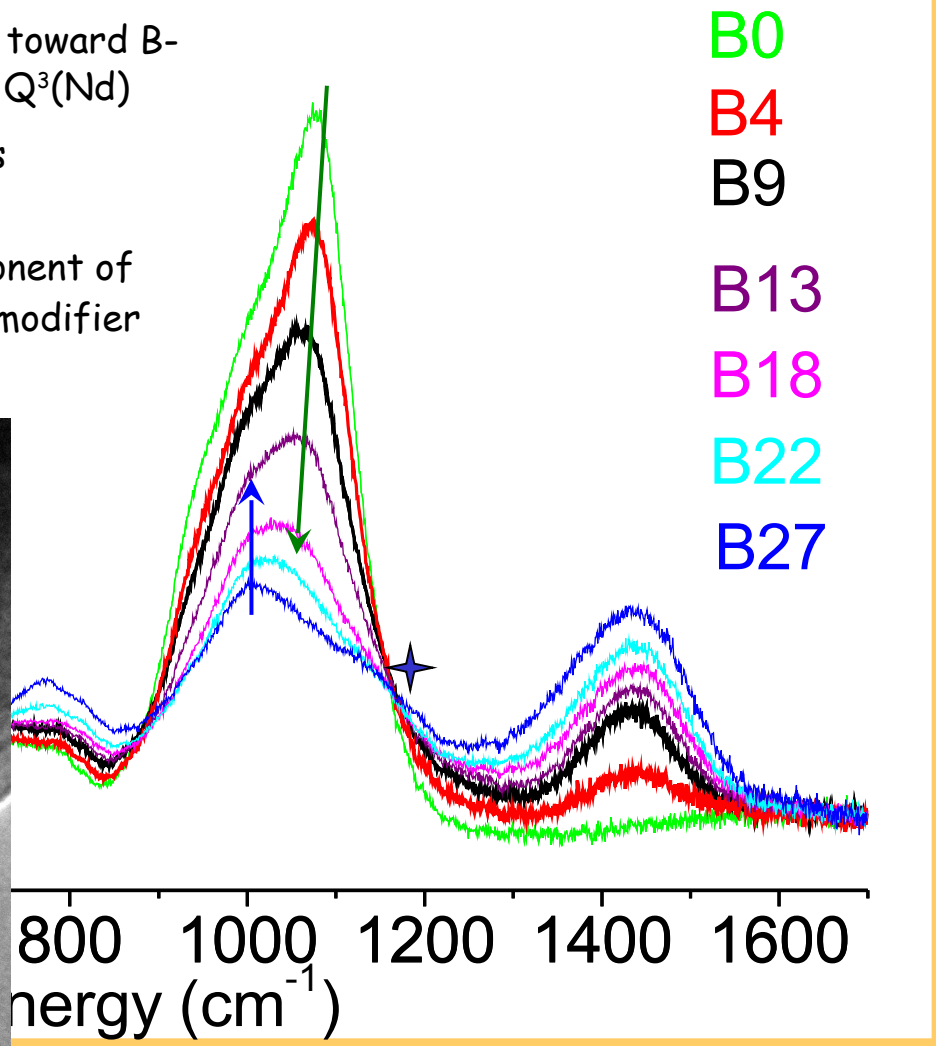
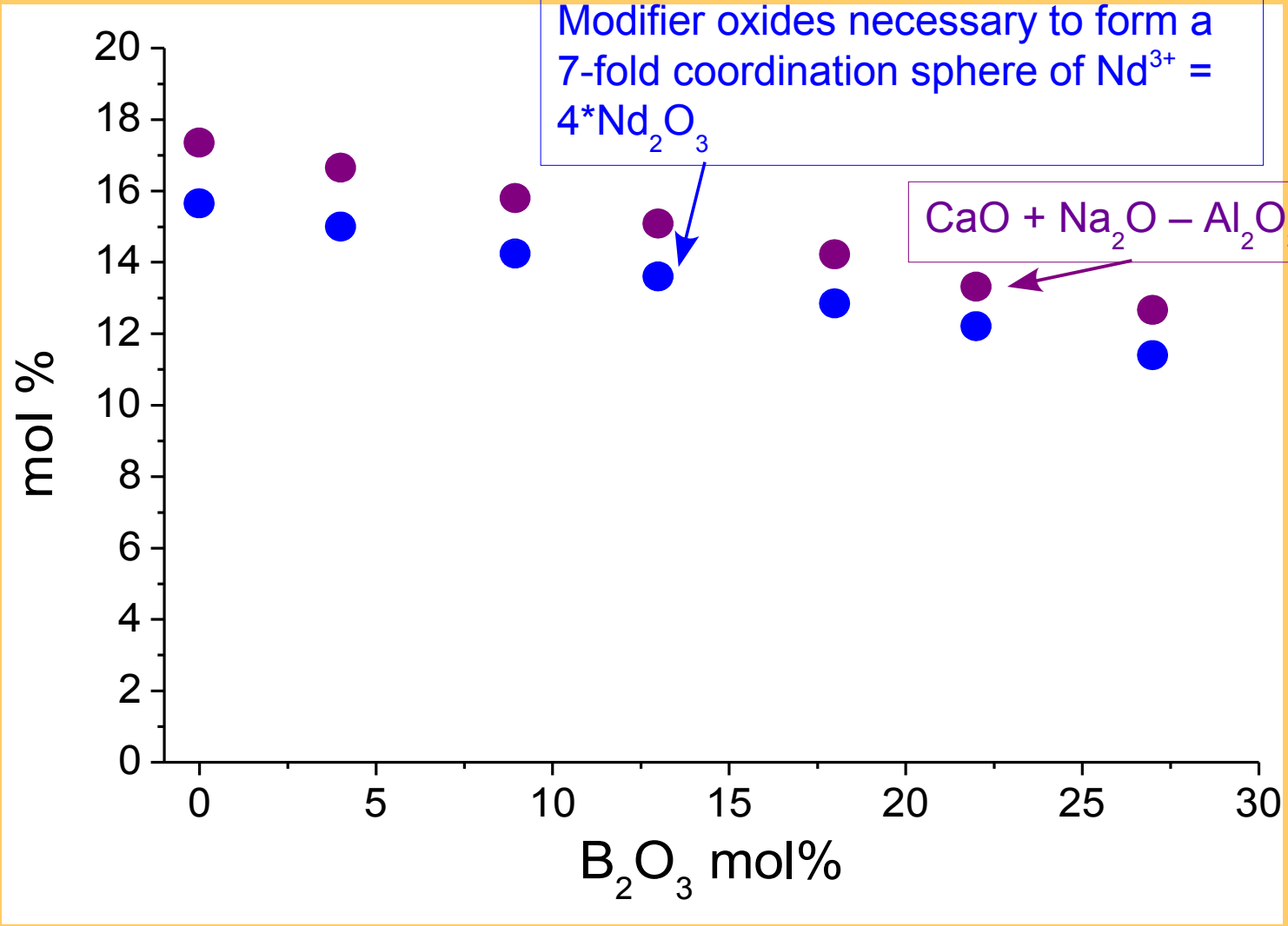




Nd^{3+} local environment : considerations from the composition



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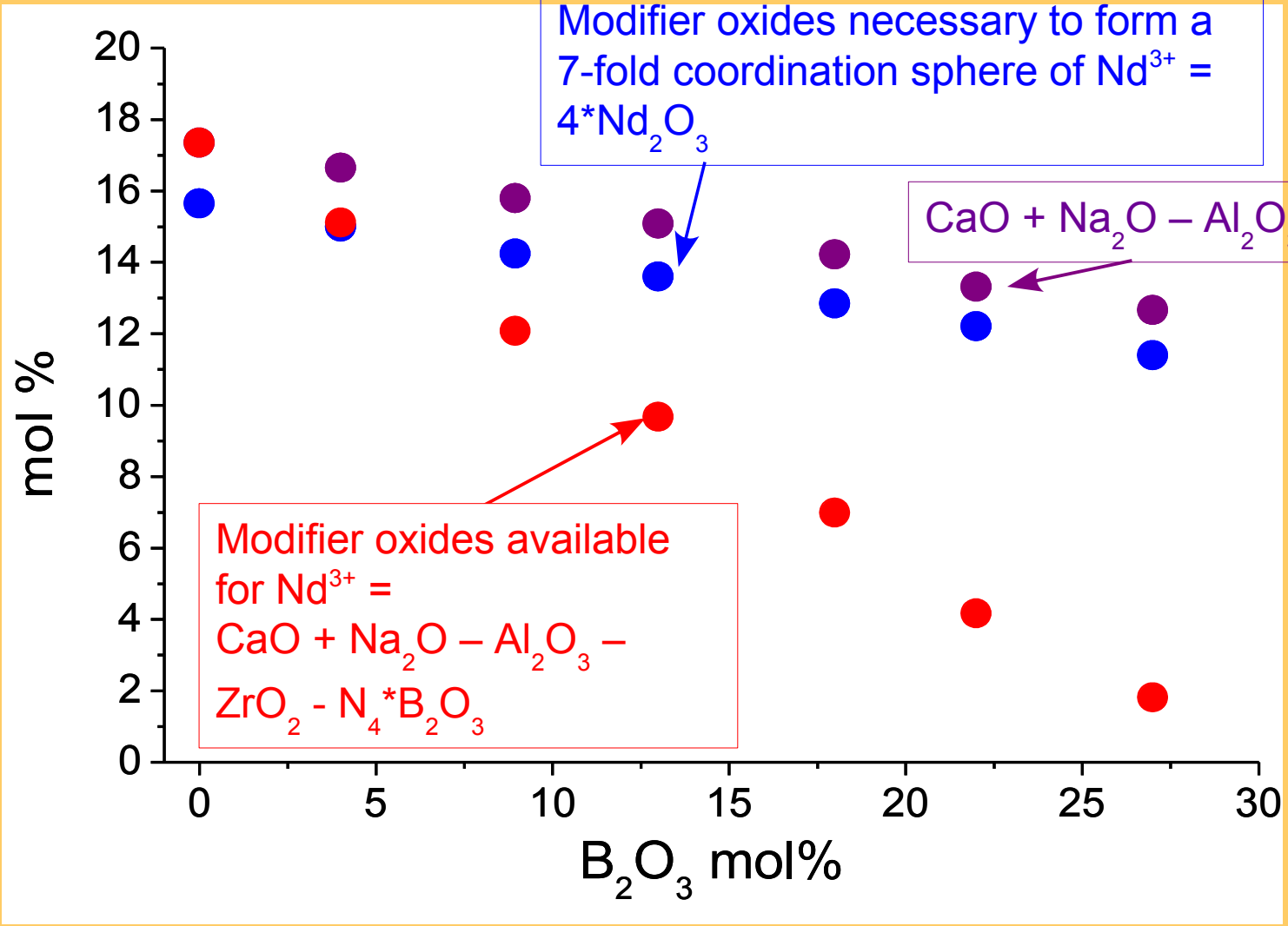

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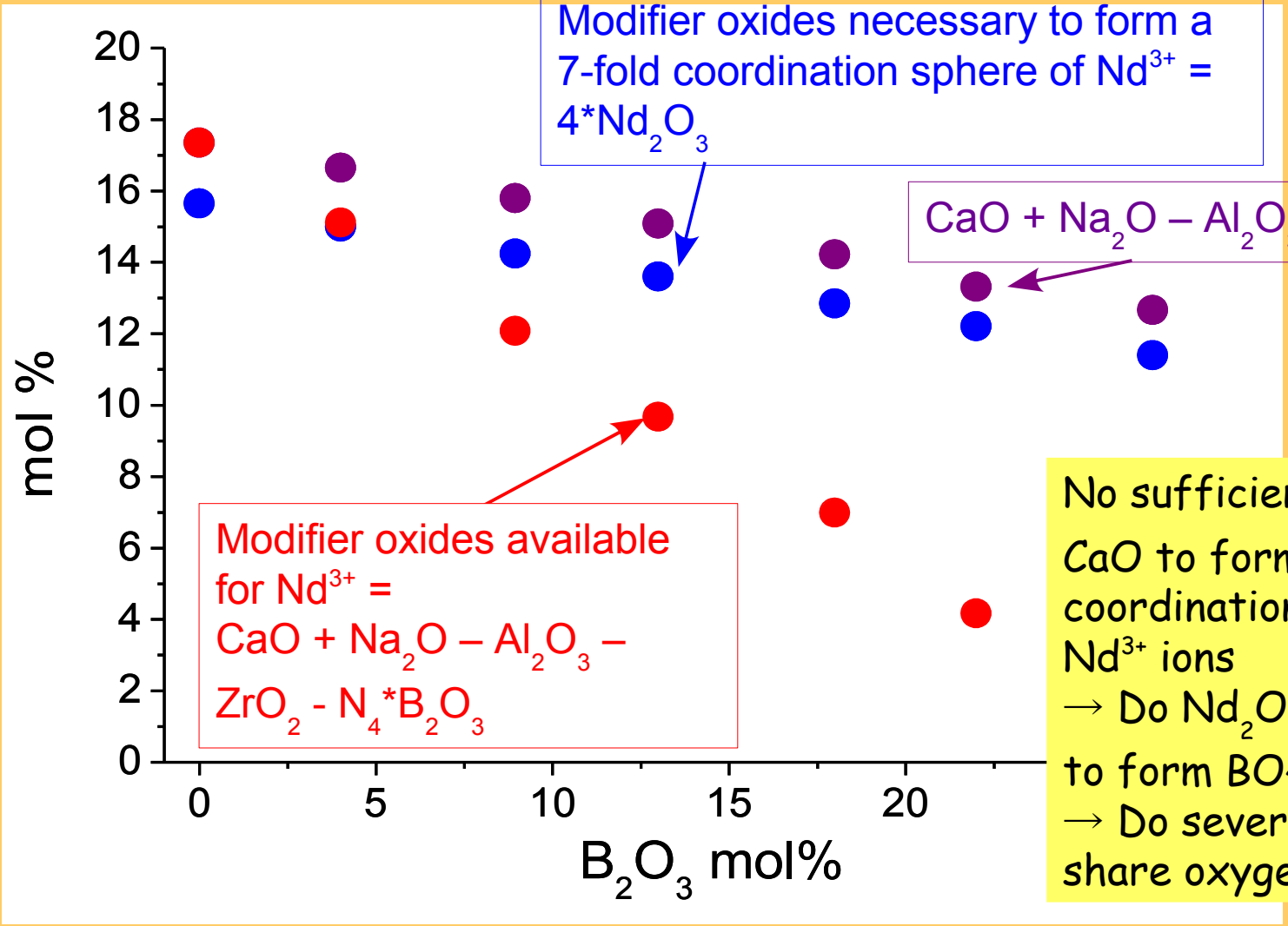
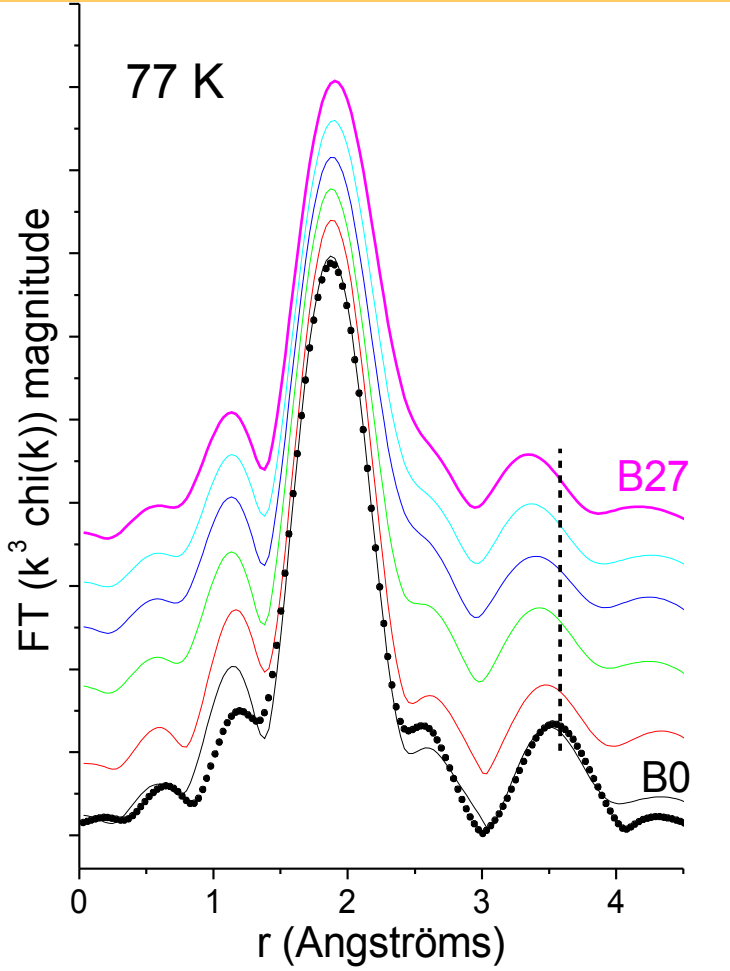


No sufficient Na_2O and CaO to form the coordination sphere of Nd^{3+} ions
→ Do Nd_2O_3 contribute to form BO4 units ?
→ Do several Nd^{3+} share oxygens ?

Nd^{3+} local environment : EXAFS at the Nd L_3-edge



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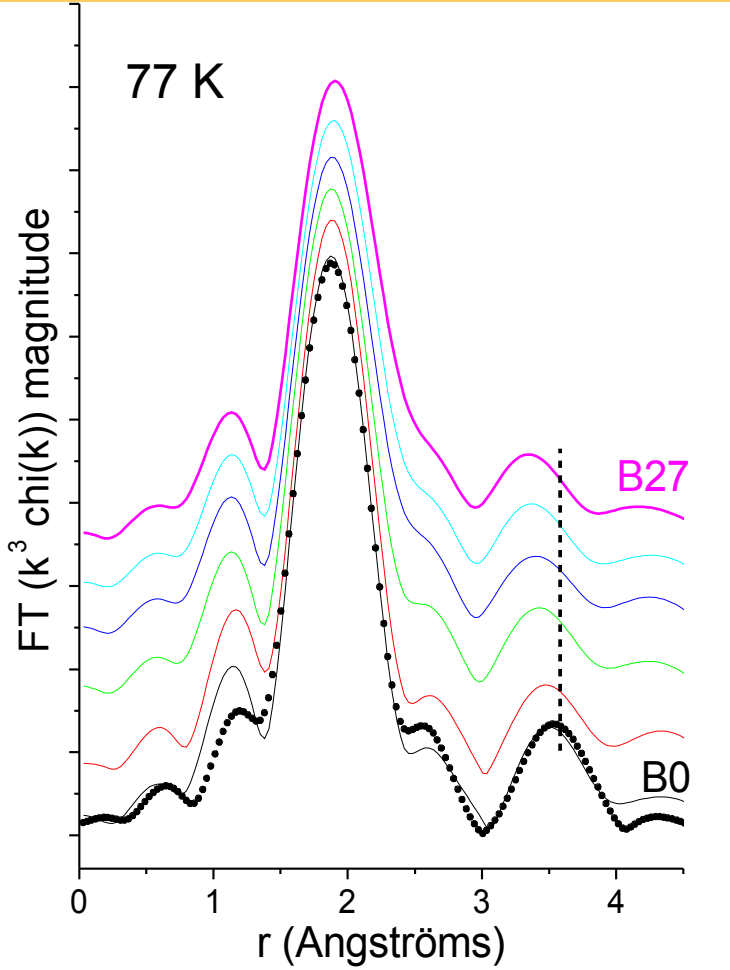

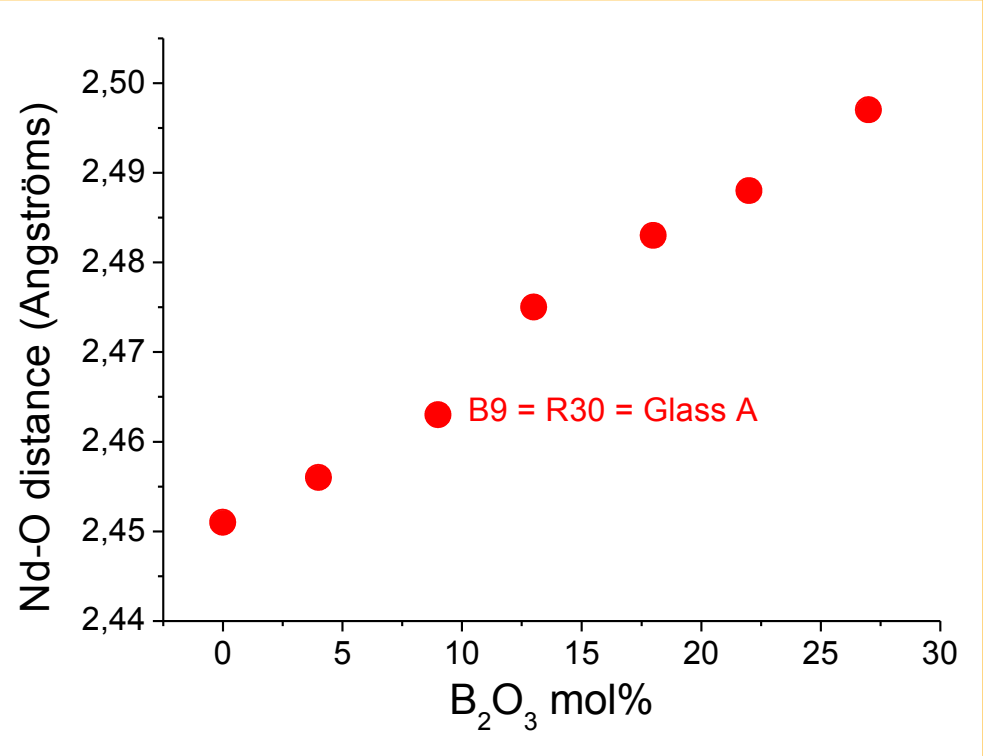

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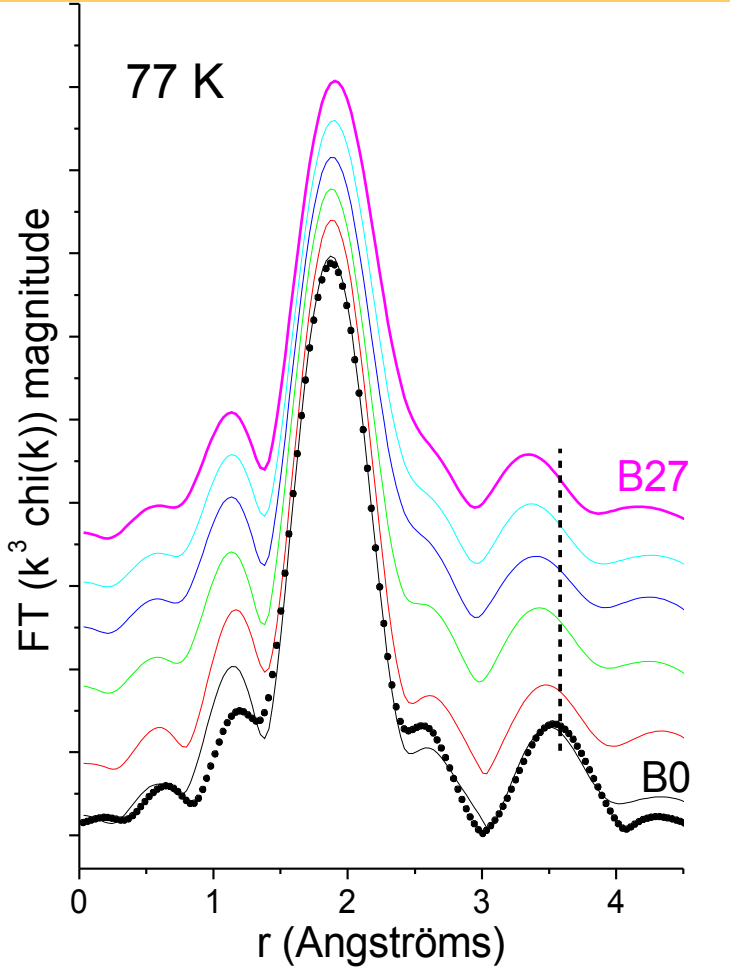

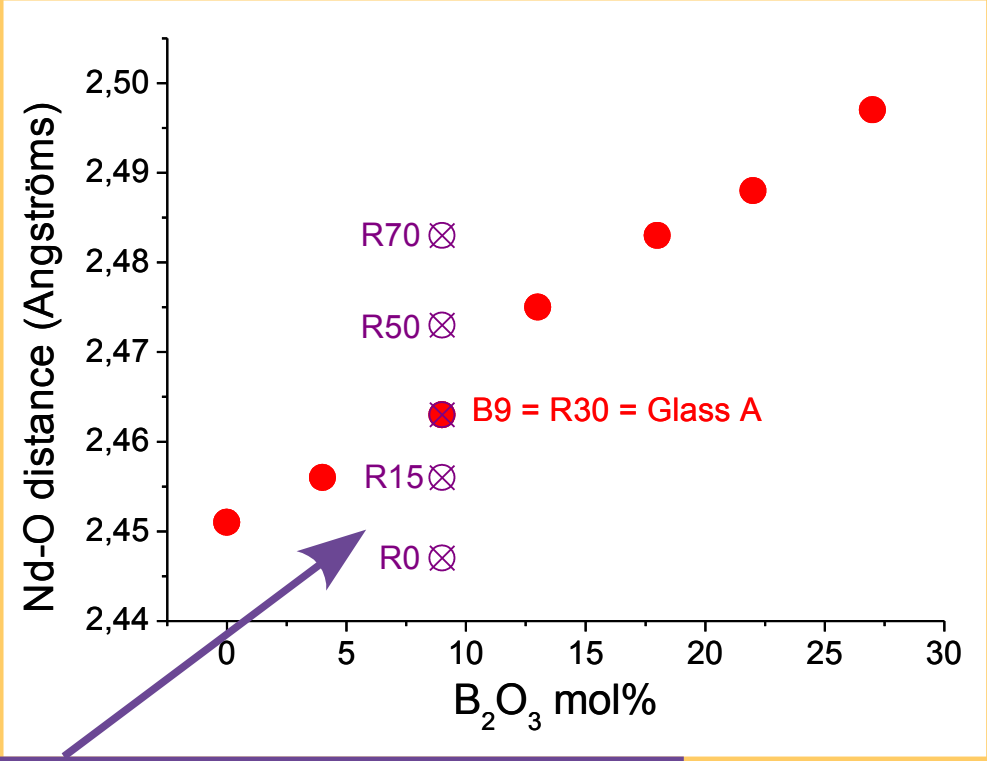

Comparison with R glass series
R = CaO / (CaO + Na_2O)

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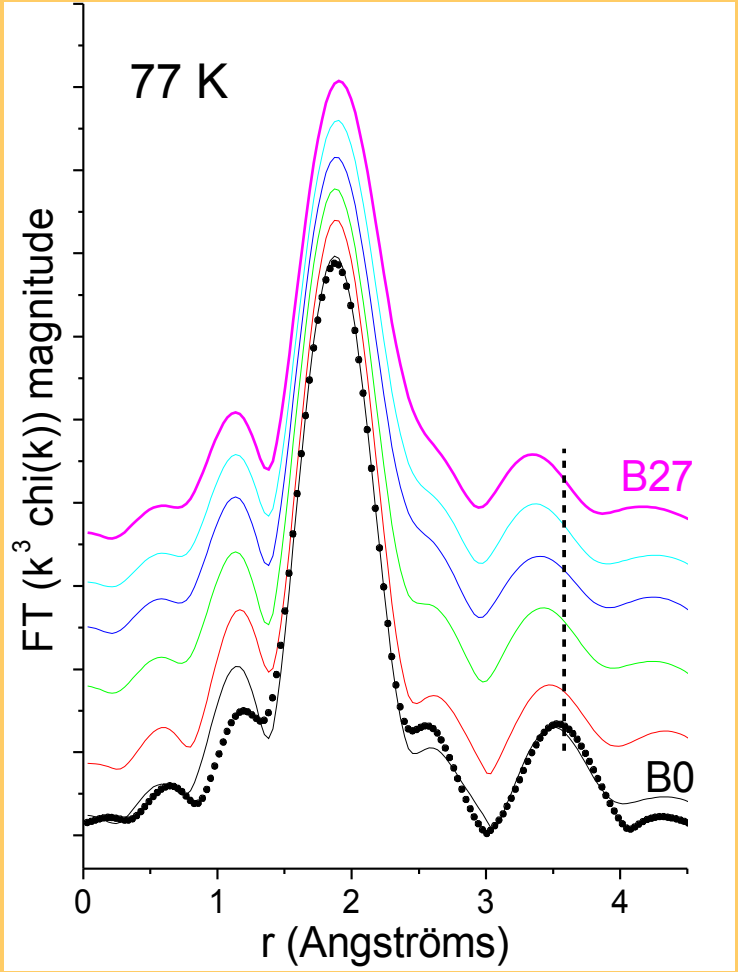

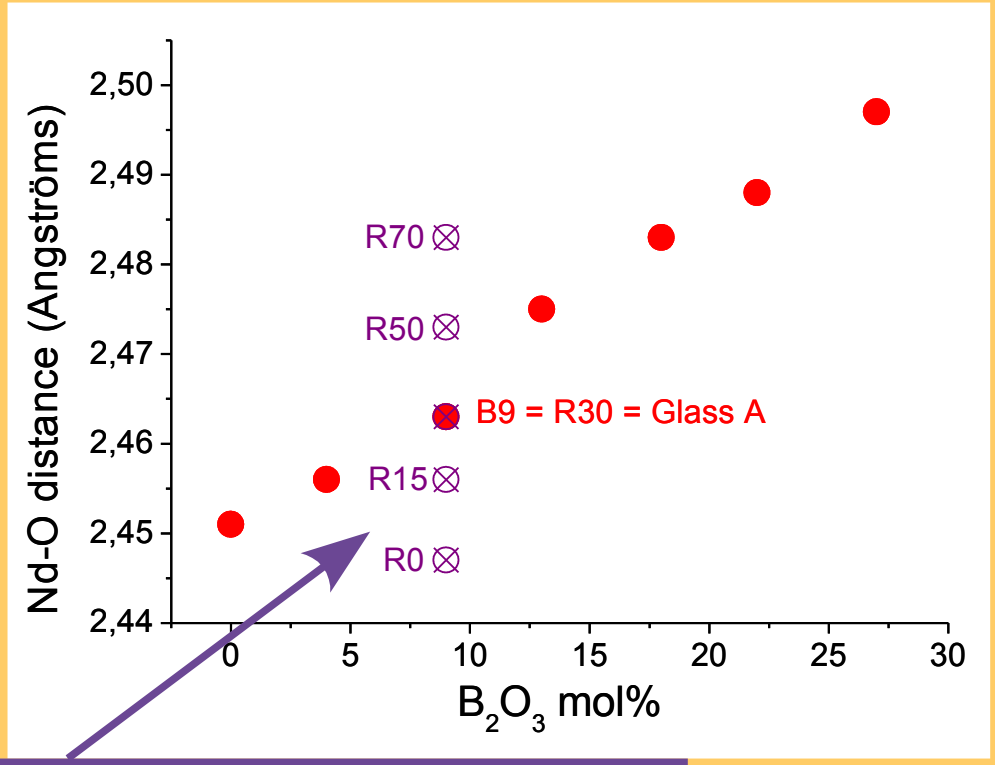

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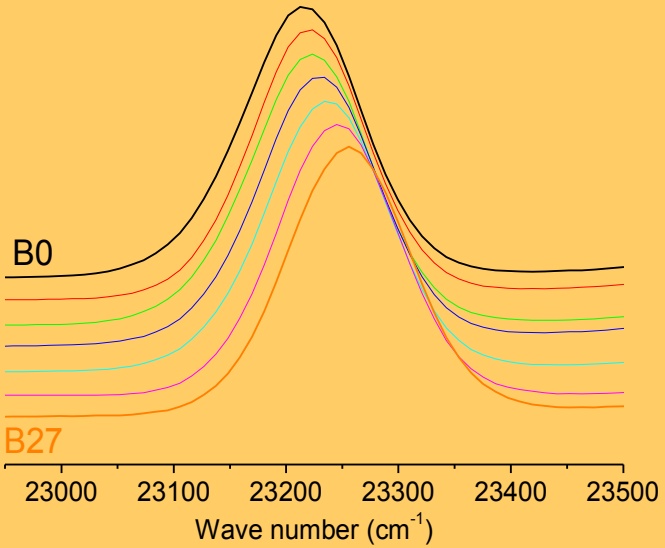
Nd-O mean distance increases with B_2O_3 content on a wider range than that due to Ca/Na substitution

Nd^{3+} local environment : optical spectroscopy

$^4I_{9/2} \rightarrow {}^2P_{1/2}$ transition at 10 K



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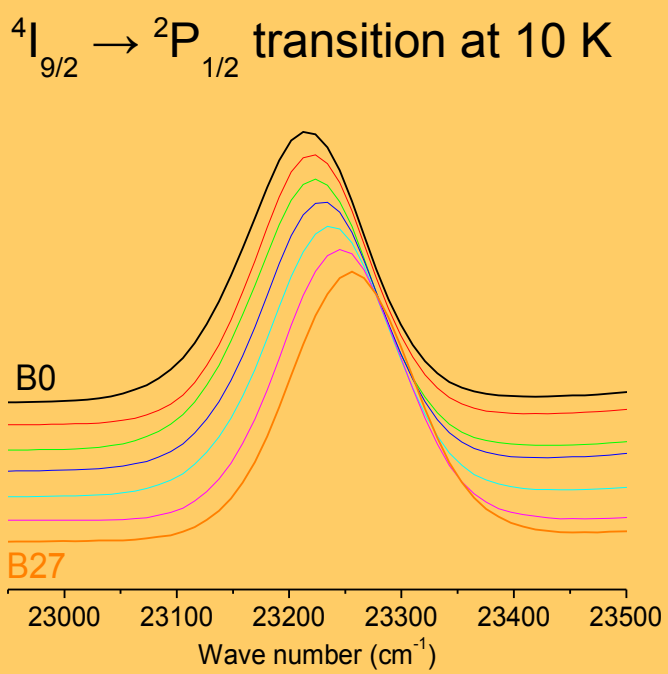

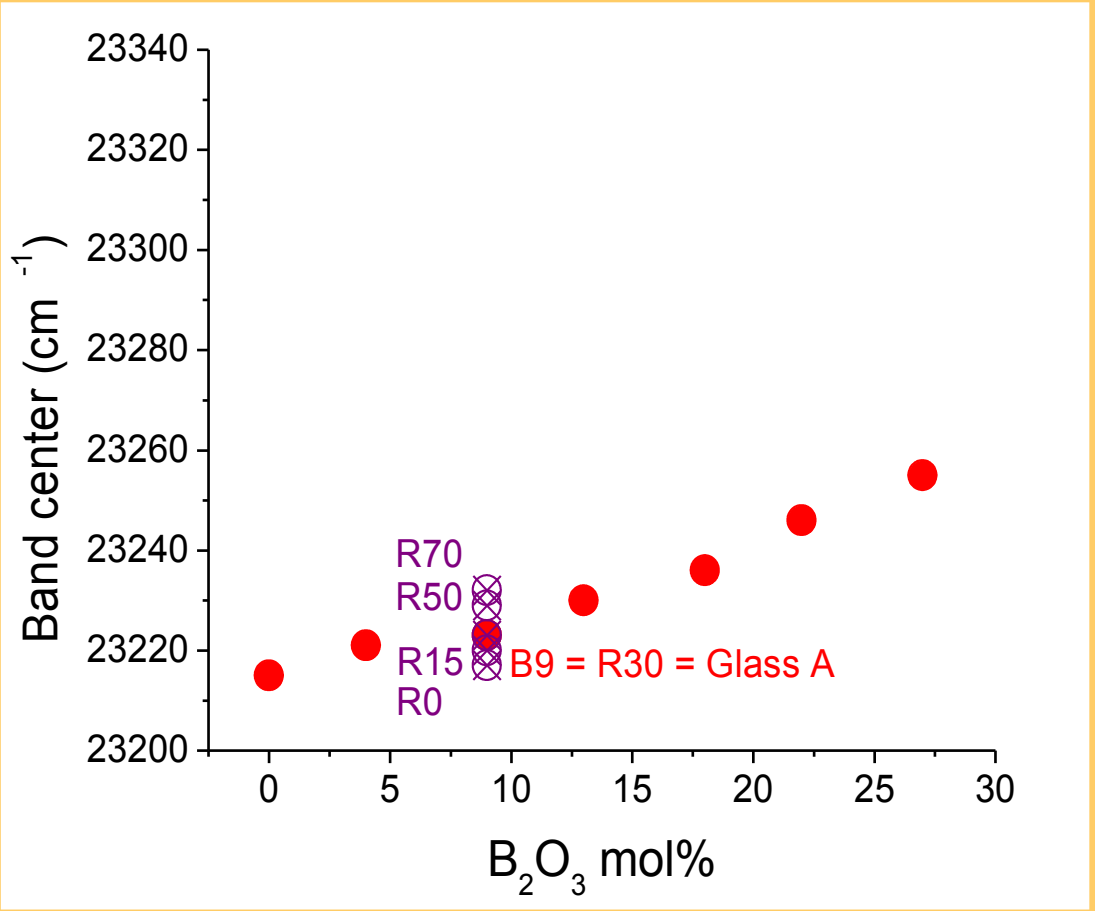

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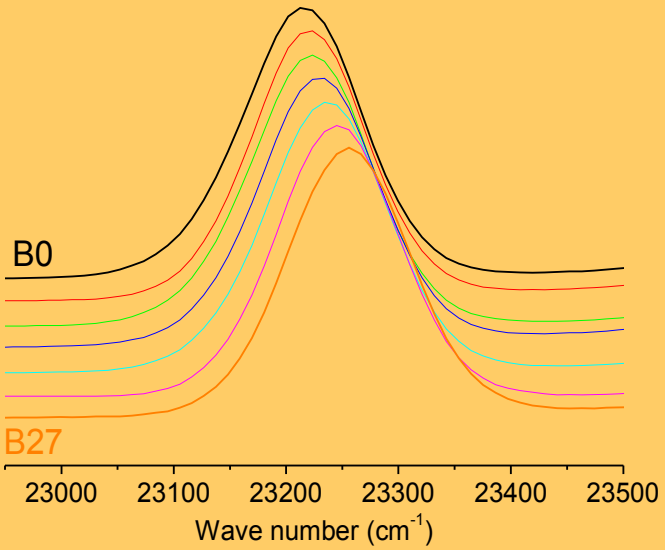
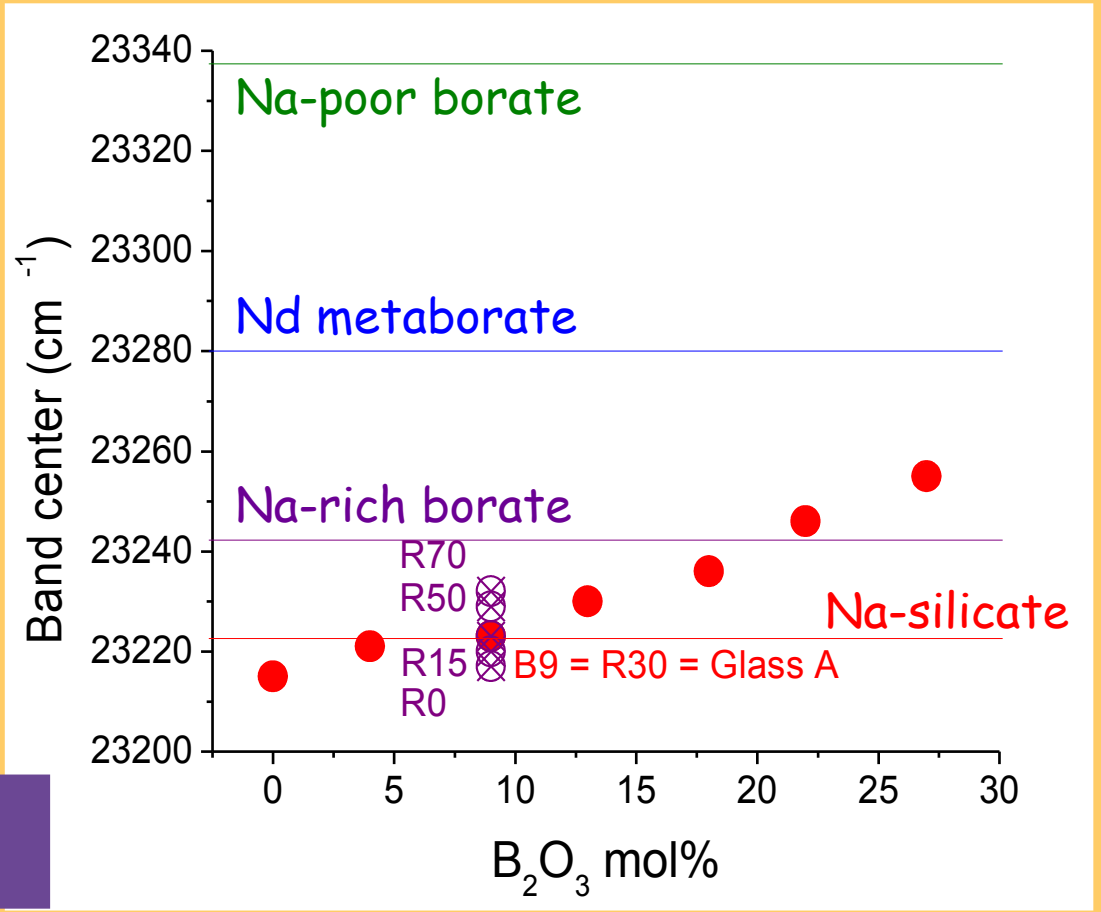


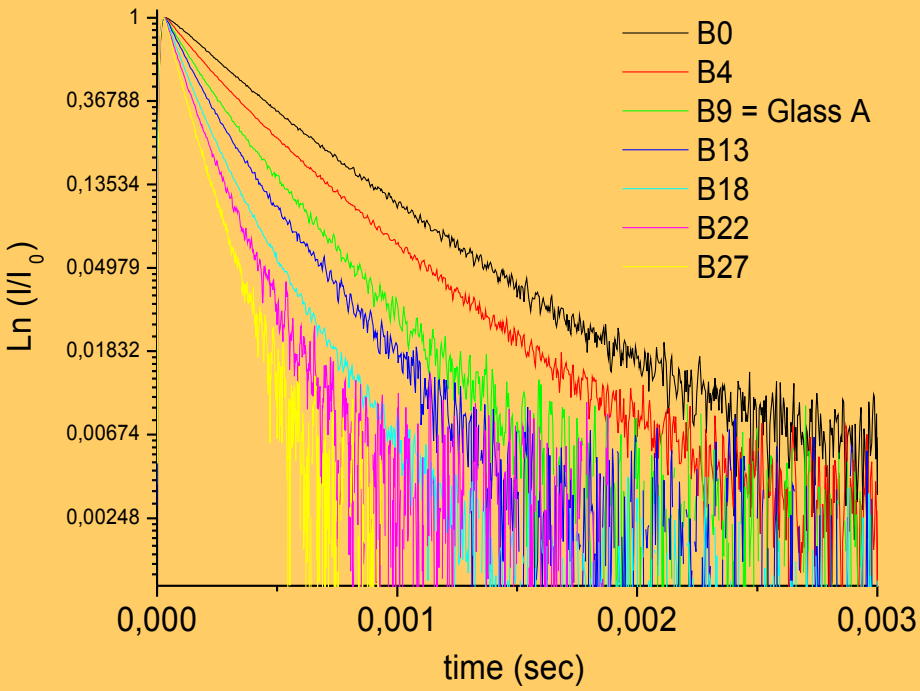


Comparison with R series and with simple model glasses

Nephelauxetic shift toward high energy consistent with dN-O increasing
At high B_2O_3 content, band center close to that of Na-rich borate environment

Nd^{3+} local environment : luminescence decays

Nd^{3+} global concentration 2.1. 10^{+19} $Nd.cm^{-3}$ for all glasses



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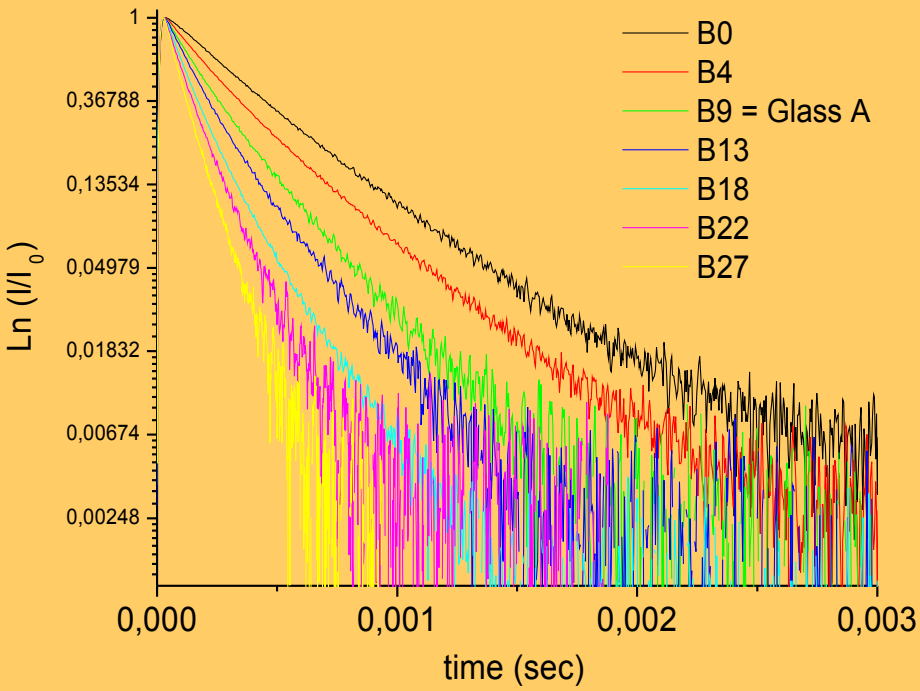

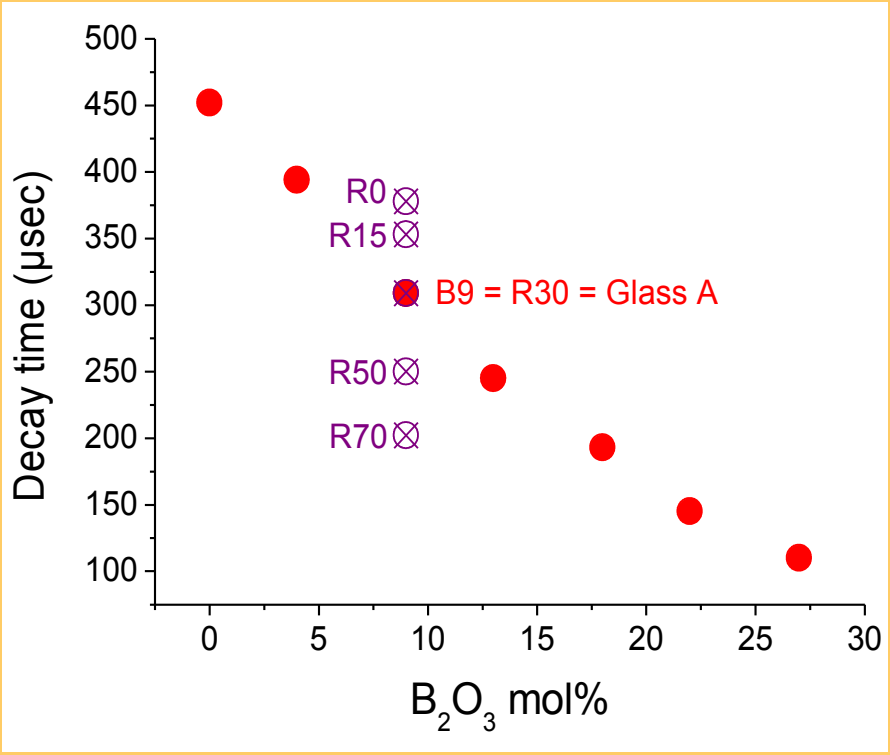

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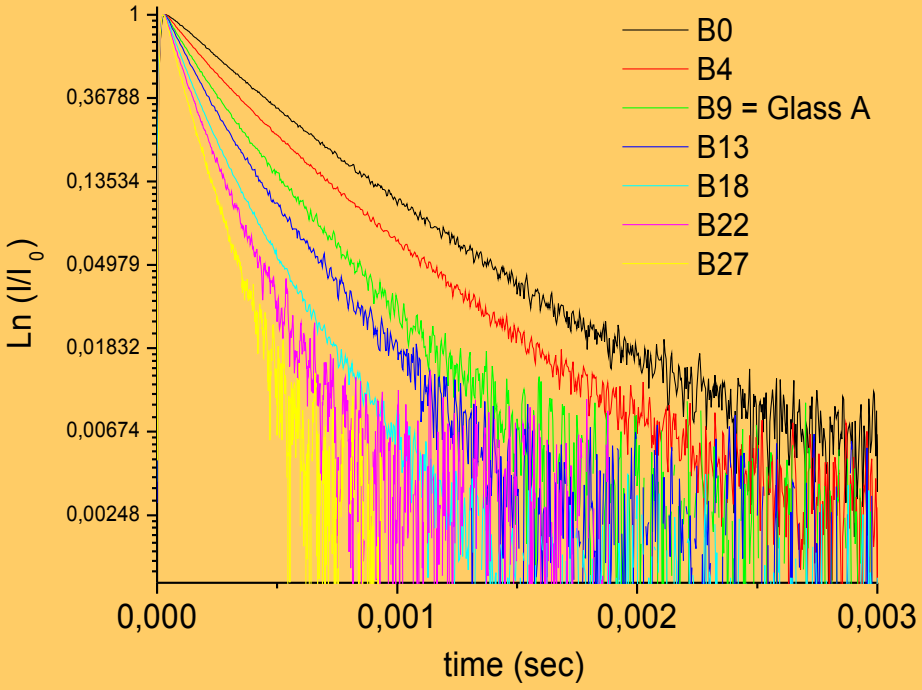
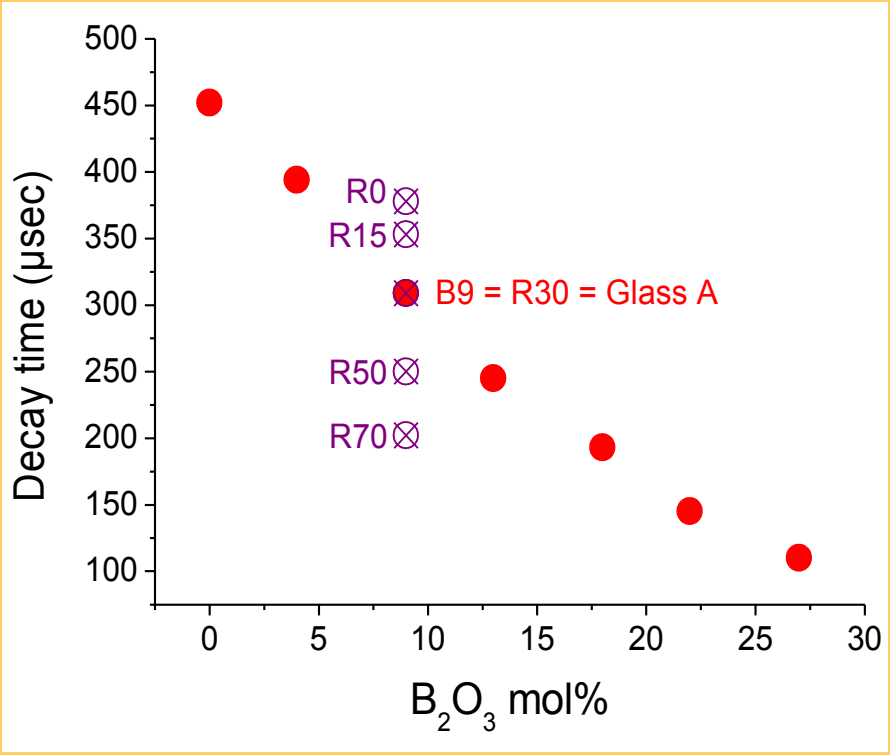




$$\frac{1}{\tau} = \frac{1}{\tau_{rad}} + W_{phonons} + W_{migration} + W_{cross-relaxation}$$

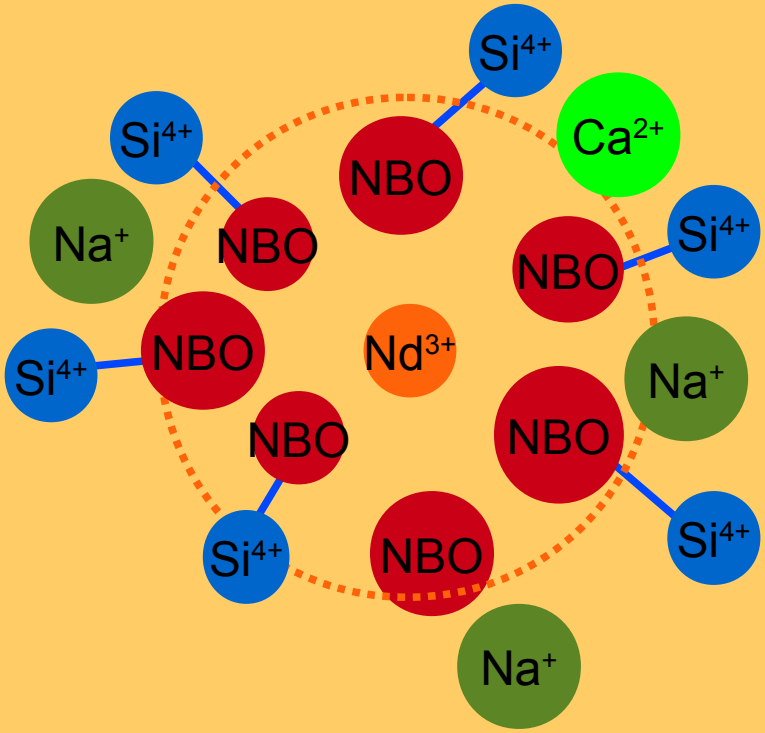
assumed identical in Bx and R series

depend on local Nd concentration

Nd^{3+} local concentration increases with B_2O_3 content

This effect is obvious even at low B_2O_3 and is not due only to Ca/Na substitution around Nd^{3+}

Summary of spectroscopic results on Nd^{3+} local environment



B0 glass : well-defined ~7-fold coordination sphere

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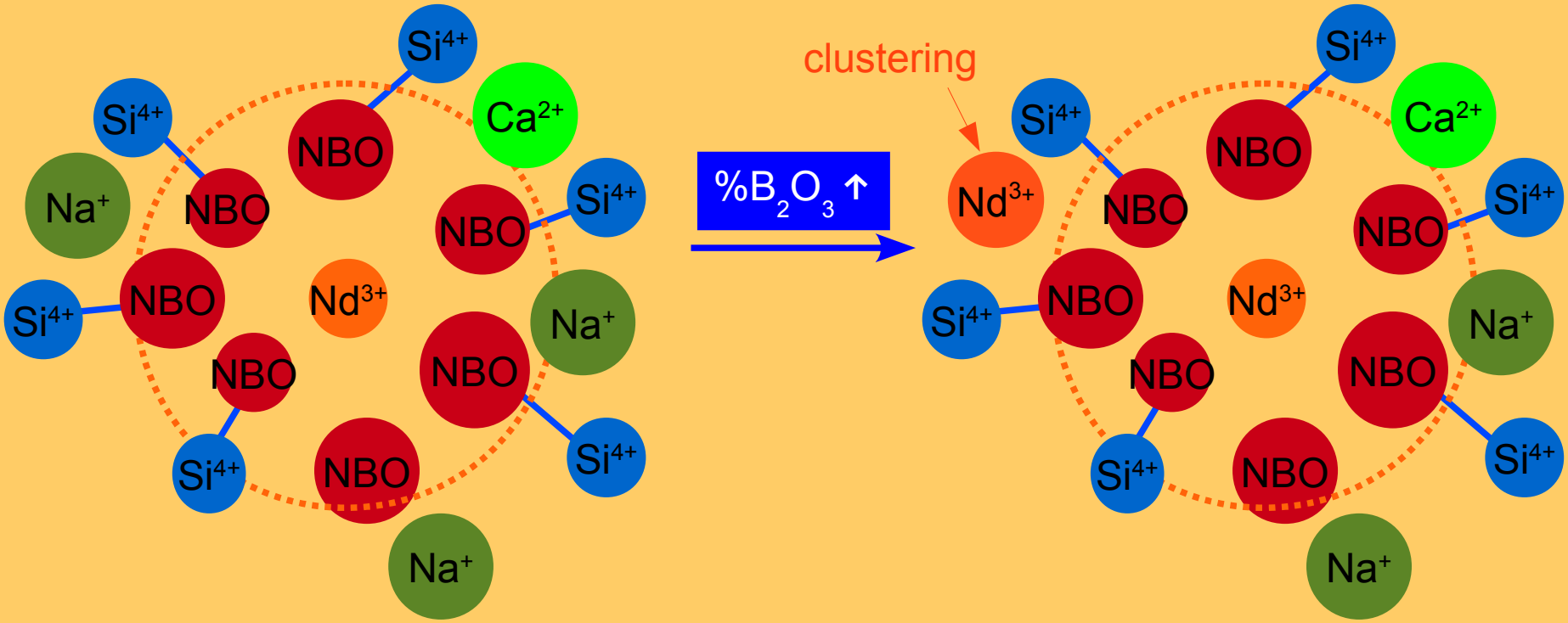

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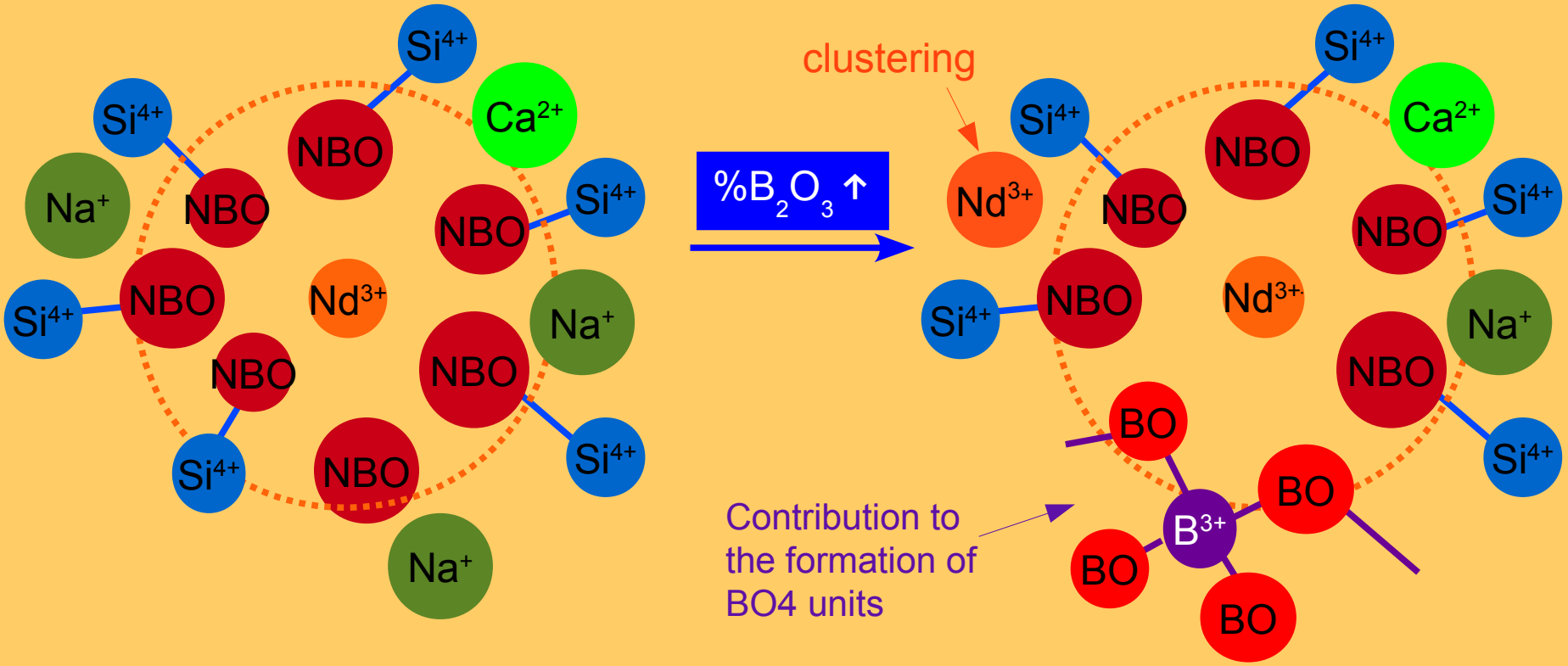

B0 glass : well-defined ~7-fold coordination sphere

Spectroscopic data can not discriminate between :
- Nd clustering and change of Ca/Na distribution around Nd
- Formation of BO4 units within a B-enriched borosilicate phase

Implications on the glass thermal stability

Slow cooling at 1°C/min

Nd^{3+} ions charge compensation by other species than Ca^{2+} and Na^{+}

⬇

Crystallization tendency of $Ca_2Nd_8(SiO_4)_6O_2$ apatite decreases

Implications on the glass thermal stability

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↓

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~~Nd clustering~~

~~Change of Ca/Na ratio around Nd~~

Nd_2O_3 reaction with B_2O_3 within a B-enriched borosilicate phase ?

Implications on the glass thermal stability

Slow cooling at 1°C/min

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Crystallization tendency of $Ca_2Nd_8(SiO_4)_6O_2$ apatite decreases

CaO and Nd_2O_3 contribute to form BO_4 units

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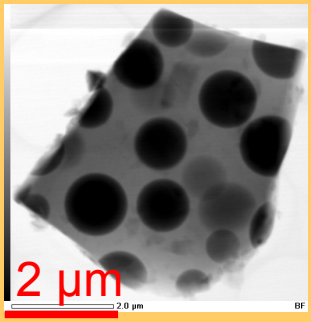
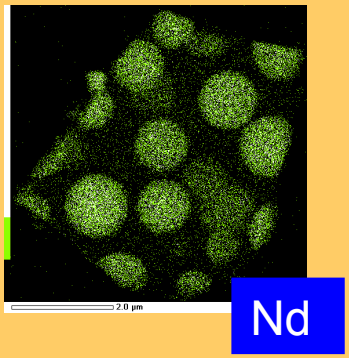
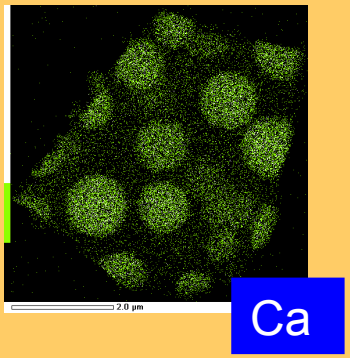
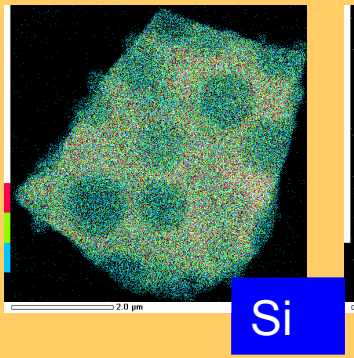
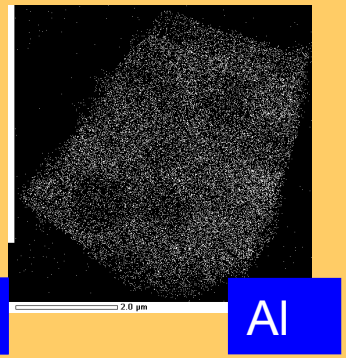


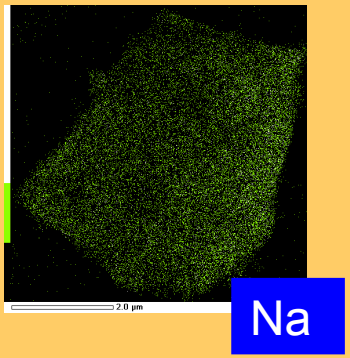
Phase separation in B18, B22 and B27 after slow cooling (1°C/min)





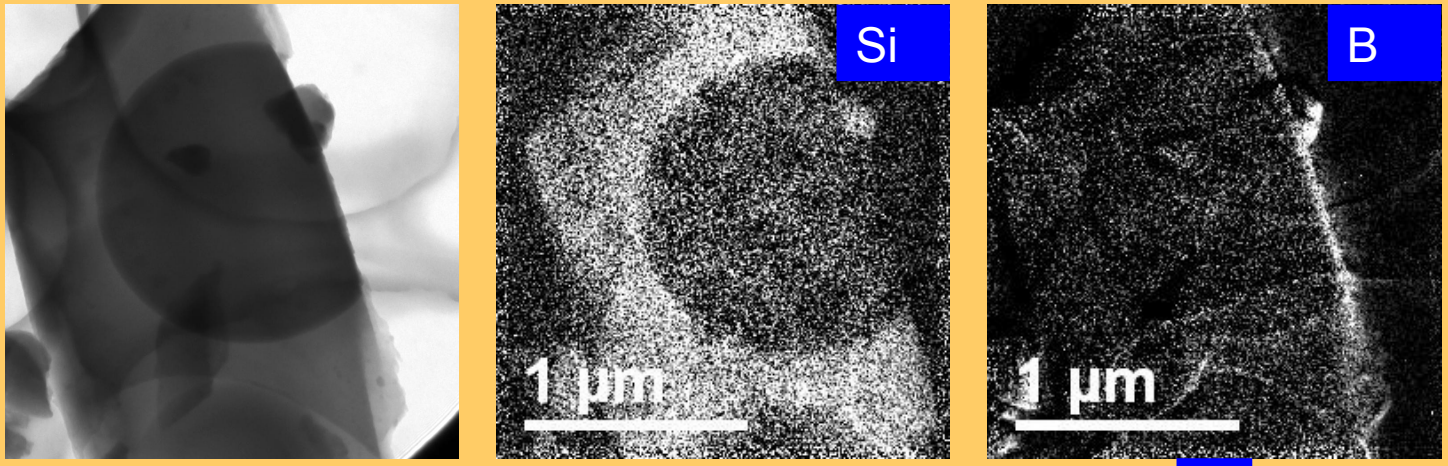






Implications on the glass thermal stability

EFTEM at the B and Si K-edges on B27 glass cooled at 1°C/min



Contrast at the Si K-edge, not at the B K-edge !
Si in excess is expelled outside the Nd- and Ca-rich phase

Conclusions

Glass A = composition range where CaO and Na_2O are not sufficient to charge-compensate all Al_2O_3, ZrO_2, B_2O_3 (as BO_4 units) and Nd_2O_3

Observation : when B_2O_3 content increases, the number of BO_4 units also increases (same proportion 40 %)

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A polymerized SiO_2 component appears at a very small scale (< TEM scale)
Nd^{3+} and Ca^{2+} cluster within a borosilicate, Si-depleted, depolymerized phase.
This is not exactly what could be inferred from extension of the Dell and Bray model (formation of a B-enriched depolymerized phase).

Questions and perspectives

- What medium-range structure for this complex inhomogeneous glass ?
  → What about the remaining boron in BO_3 units ? How are they accomodated in the silicate polymerized component ? Does CaO and Nd_2O_3 also depolymerize BO_3 units ?
  → Are there borate rings or superstructural units ?
- Is the reaction of Nd_2O_3 with B_2O_3 (forming BO_4 units and maybe depolymerized BO_3 units) only due to the lack of modifier ions in this particular composition range?
  ...Or is it a preferential reaction occuring even at larger Na_2O, CaO contents ?

Need for « medium-range order sensitive tools » (simulations, NMR...) for the study of rare earth-rich alkali borosilicate glasses...

Thank you for your attention !

Thanks to

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