Nd^{3+} environment and solubility in aluminoborosilicate glasses

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Context : research for nuclear glasses with high waste loading

• Rare earths (RE) are a significant part of the fission products (FP) and good simulants of trivalent actinides
• RE oxide concentration is ~ 4 wt% in the current nuclear glass (R7T7). It will amount to ~ 10 wt% in future nuclear glasses with higher waste loading

Chemical family	weight (kg/U)
Alkalis (Cs, Rb)	3
Alkaline-earths (Sr, Ba)	2.4
Rare-earths	**10.2**
Transition metals (Mo, Zr, Tc)	7.7
Chalcogens (Se, Te)	0.5
Halogens (I, Br)	0.2
Noble metals (Ru, Rh, Pd)	3.9
Others (Ag, Cd, Sn, Sb…)	0.1

Main families of FP in UO_2 spent fuel initially enriched with 3.5% ^{235}U

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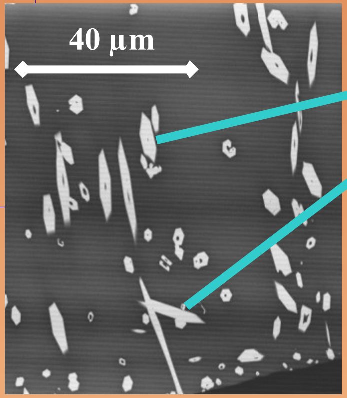
New glass compositions must avoid crystallization of big crystals during melt cooling



$Ca_2RE_8(SiO_4)_6O_2$

MA

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Aims of the study and method

- Characterizing the Nd^{3+} environment in a model glass (A)
- Studying the impact of Nd_2O_3 content on the aluminoborosilicate network structure and on the crystallization properties
- Draw structure – crystallization relationships and test compositional variations to improve the solubility of Nd^{3+} in the glass

Model glass A (mol%) :

SiO_2	Al_2O_3	B_2O_3	Na_2O	CaO	ZrO_2	Nd_2O_3
61.8	3.0	9.0	14.4	6.3	1.9	3.6

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Use of glass series and spectroscopic tools (NMR, Raman, Vis absorption, EXAFS)

- Simple reference glasses
- CaO/Na_2O ratio and alkali type
- Nd_2O_3 content from 0 to 30 wt% (7.5 mol%)

} Focus on the Nd^{3+} environment and crystallization

Nd^{3+} environment in the model glass

Reference glasses

Glass	Composition (mol%)
Na-silicate	74.38 SiO_2 - 21.29 Na_2O - 4.33 Nd_2O_3
Na-rich borate	64 B_2O_3 - 35 Na_2O – 1 Nd_2O_3
Na-poor borate	79 B_2O_3 - 20 Na_2O - 1 Nd_2O_3
Nd aluminosilicate	75 SiO_2 - 15 Al_2O_3 - 10 Nd_2O_3
Nd metaborate	75 B_2O_3 - 25 Nd_2O_3

NBO's

BO's and NBO's

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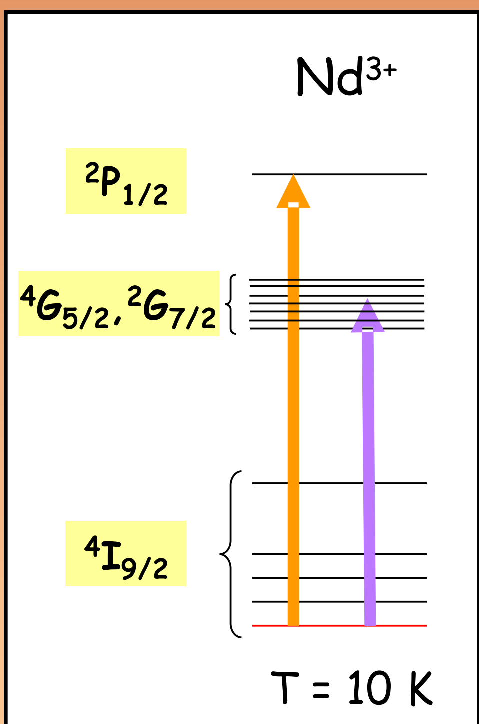
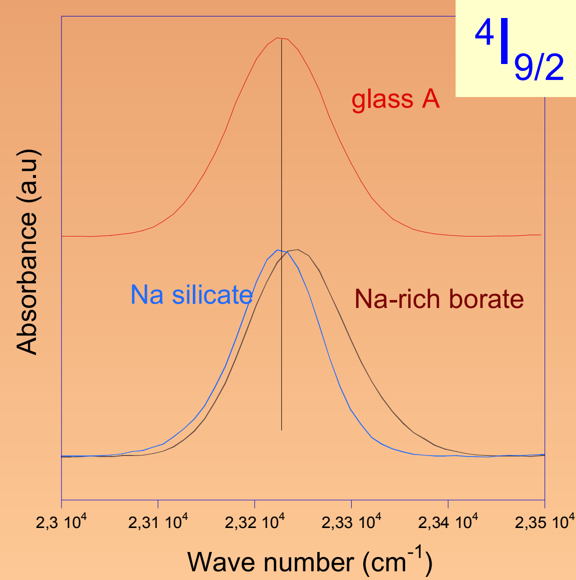
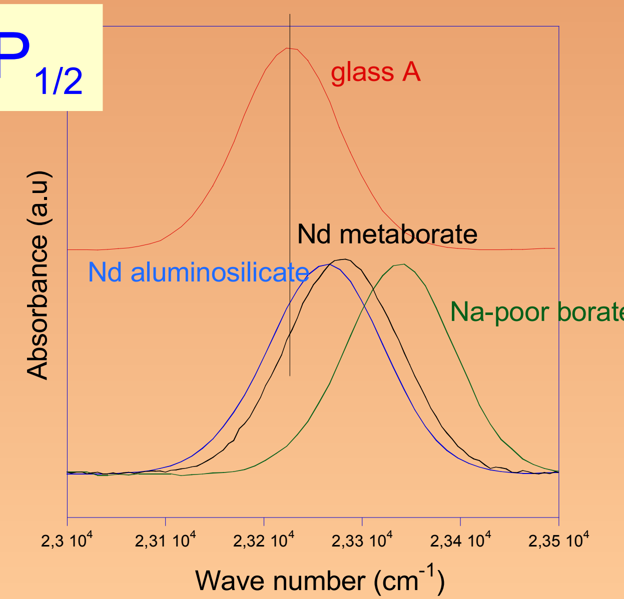


Study by optical absorption spectroscopy at low temperature

(Gatterer et al. JNCS 231 (1998) 189; Dymnikov et al. JNCS 215 (1997) 83)

$^4I_{9/2} \rightarrow ^2P_{1/2}$





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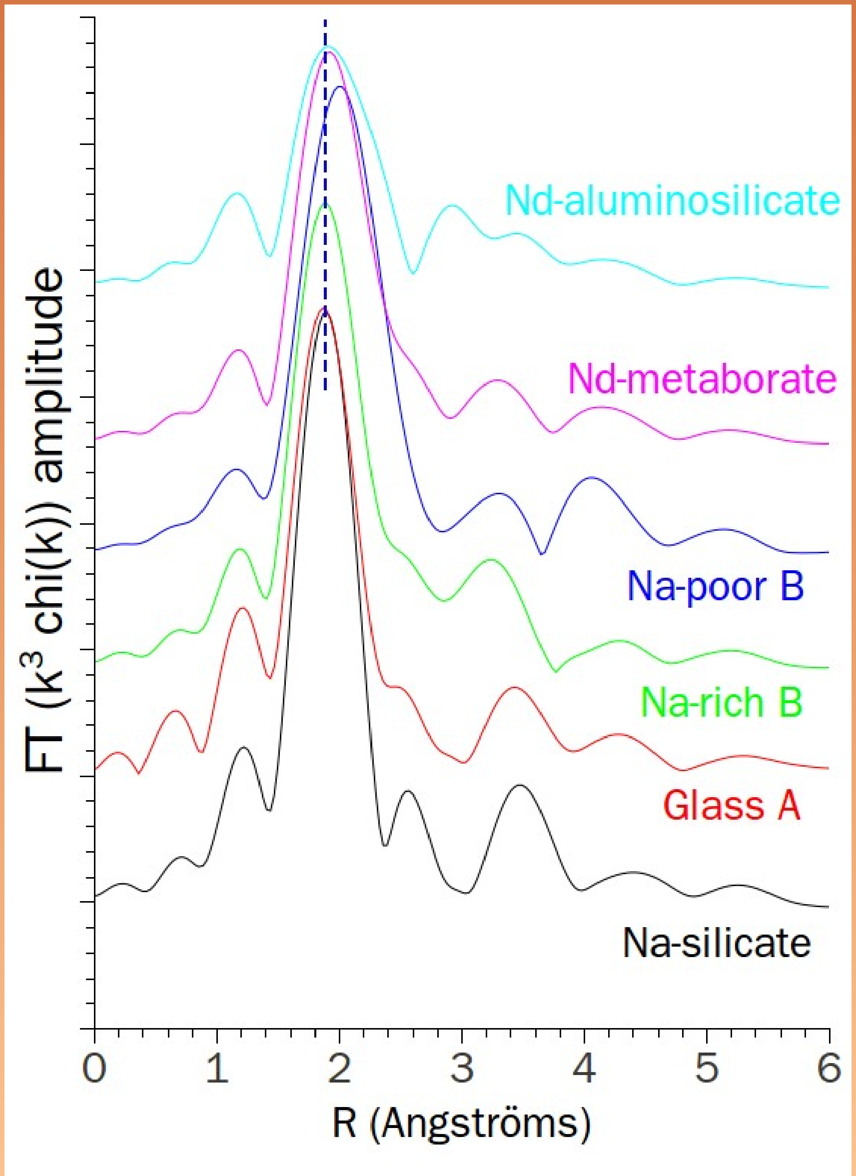
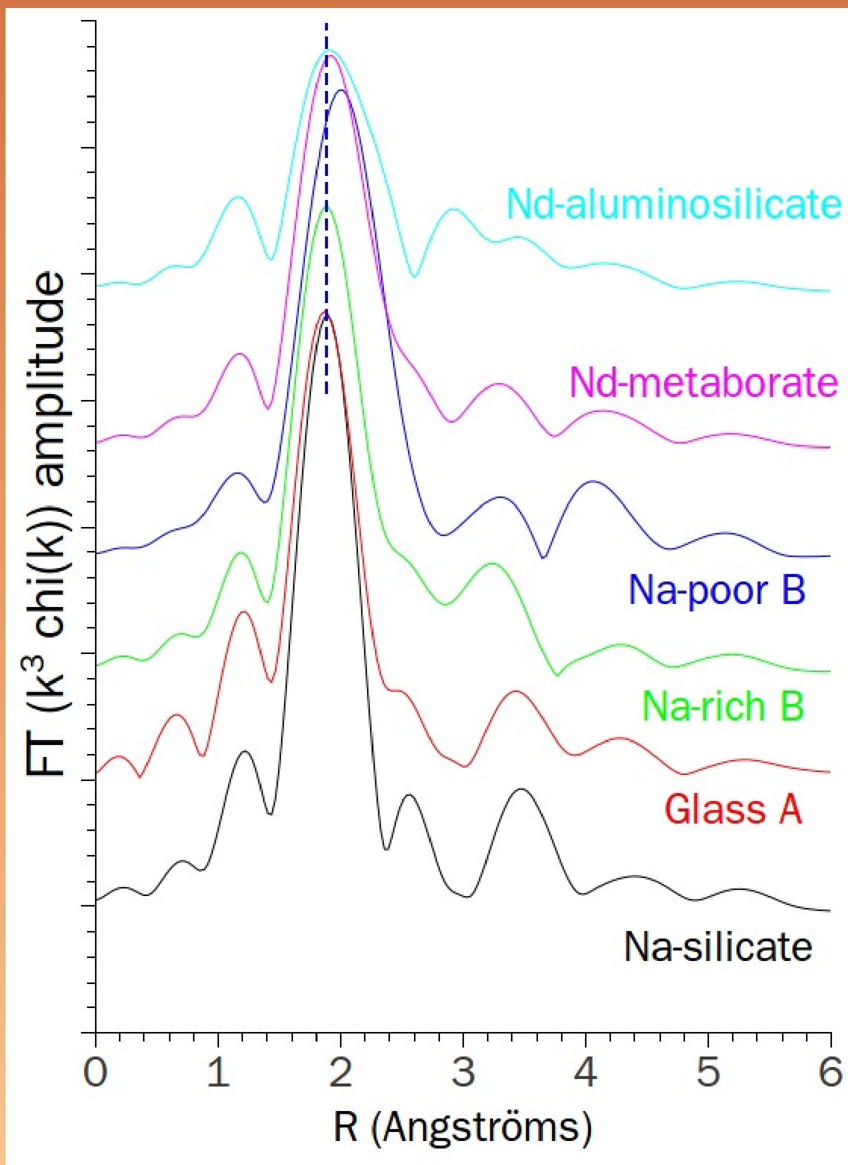


NBO rich-environment

Nd L_3-edge EXAFS at 77 K

Nd^{3+} environment in the model glass



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NBO rich-environment

- Well-defined coordination sphere
- 6 to 8 NBO's
- Mean dNd-O between 2.44 Å and 2.50 Å depending on Ca^{2+}/Na^{+} ratio or alkali type
- Consistency between dNd-O bond distance and nephelauxetic effect

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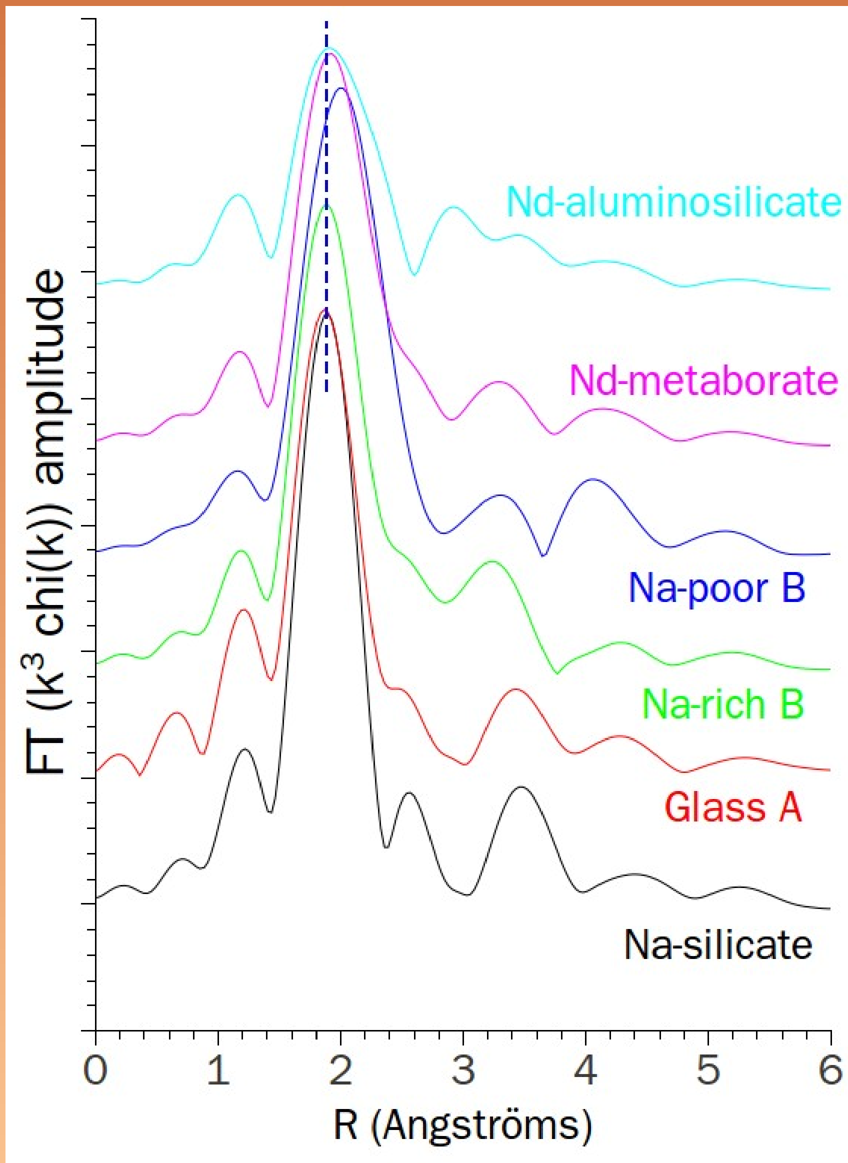

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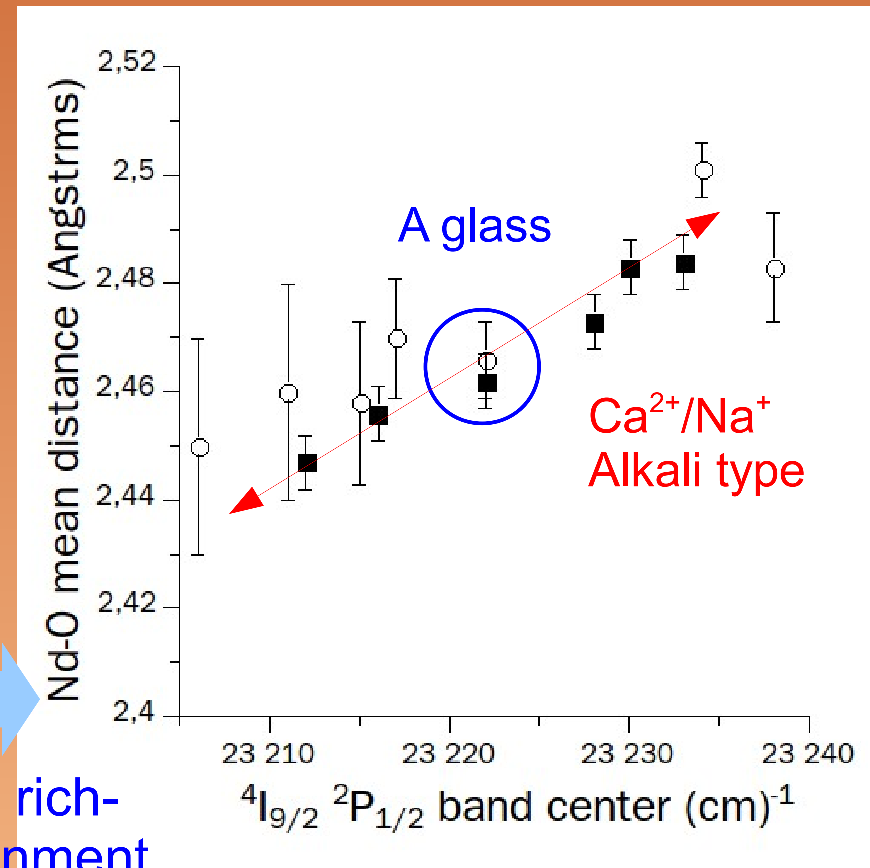

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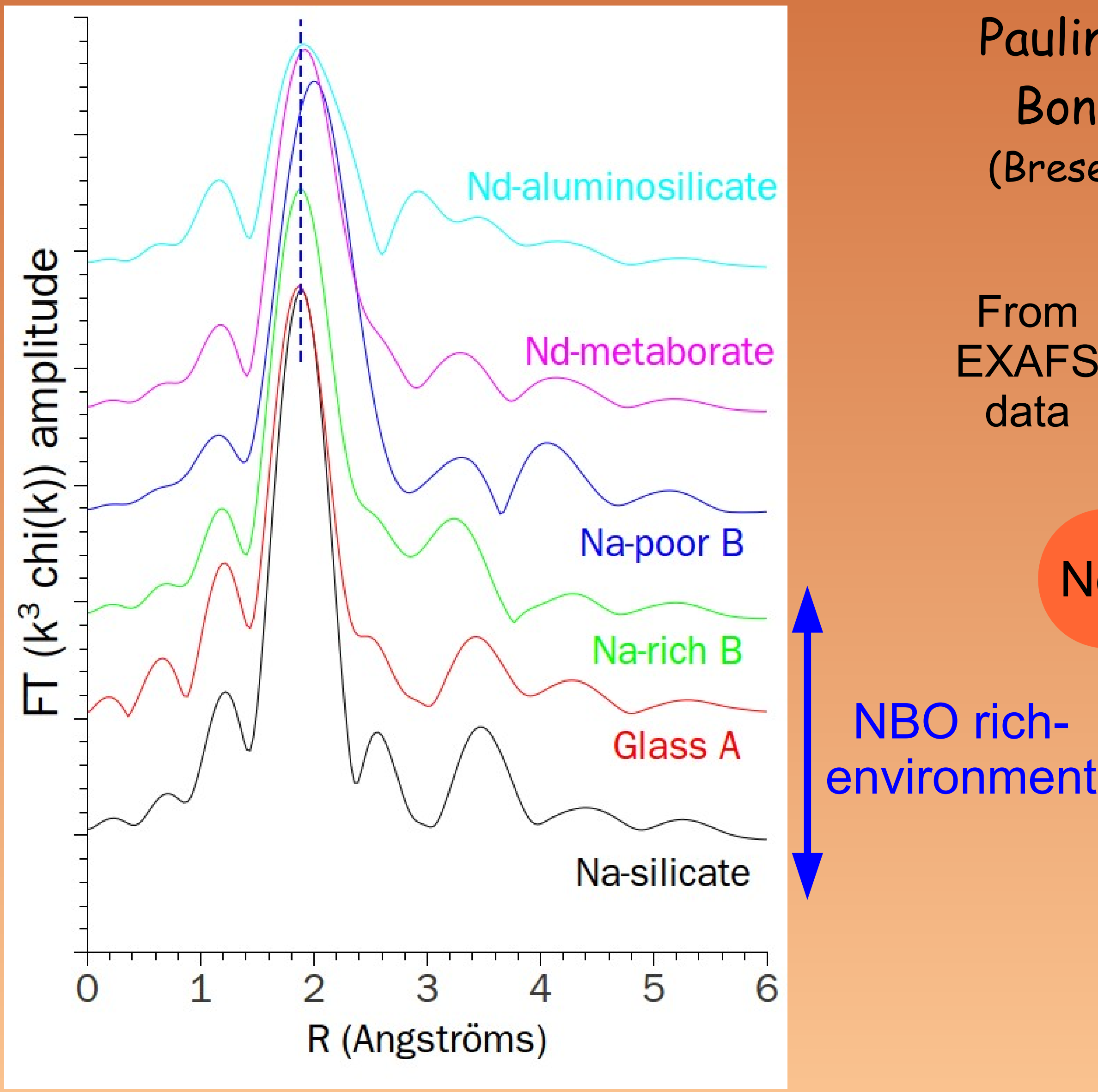

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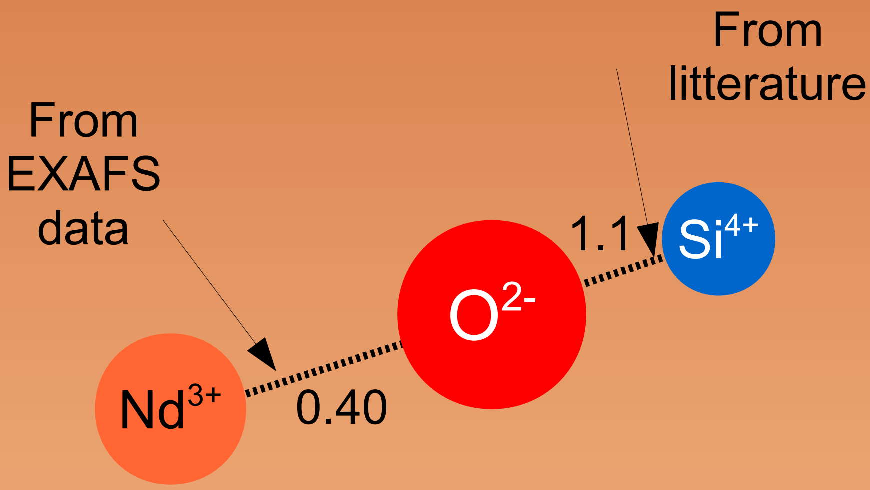
Pauling rules and Bond Valence –
Bond Length model of oxides
(Brese & O'Keefe, Acta Cryst. B, 1991)



Majérus et al., JNCS 2008

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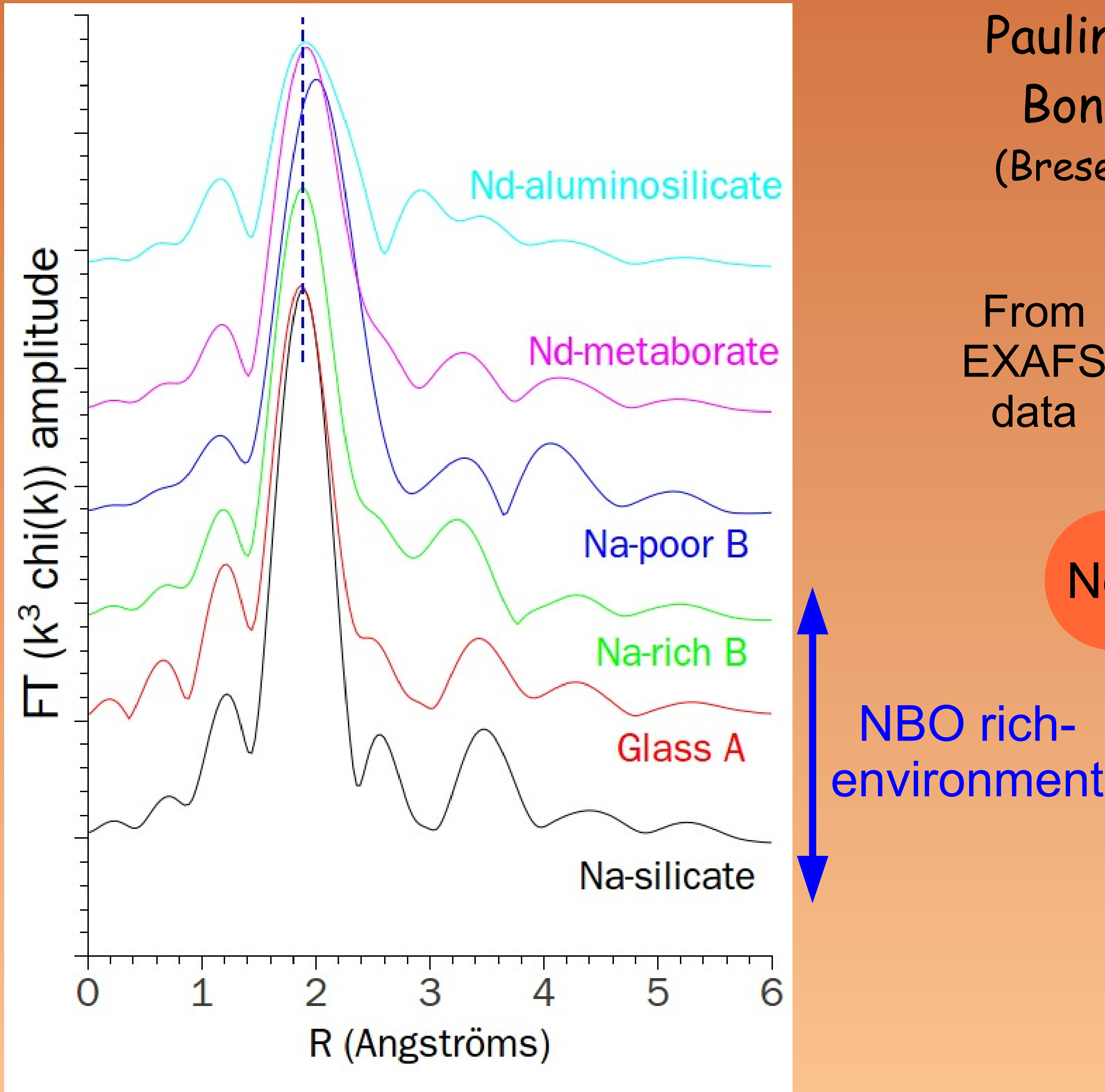

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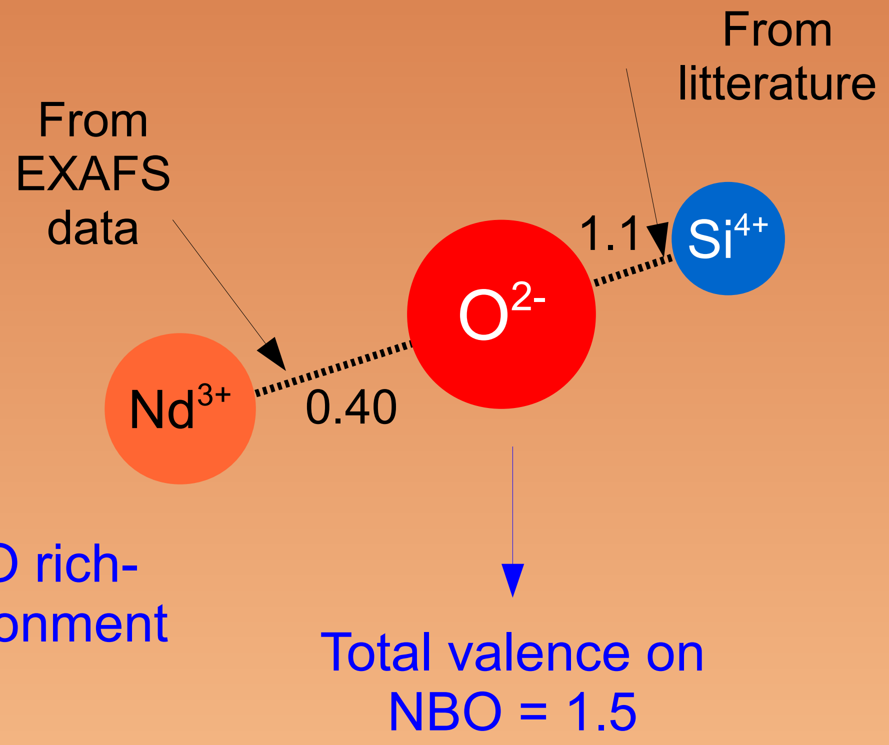

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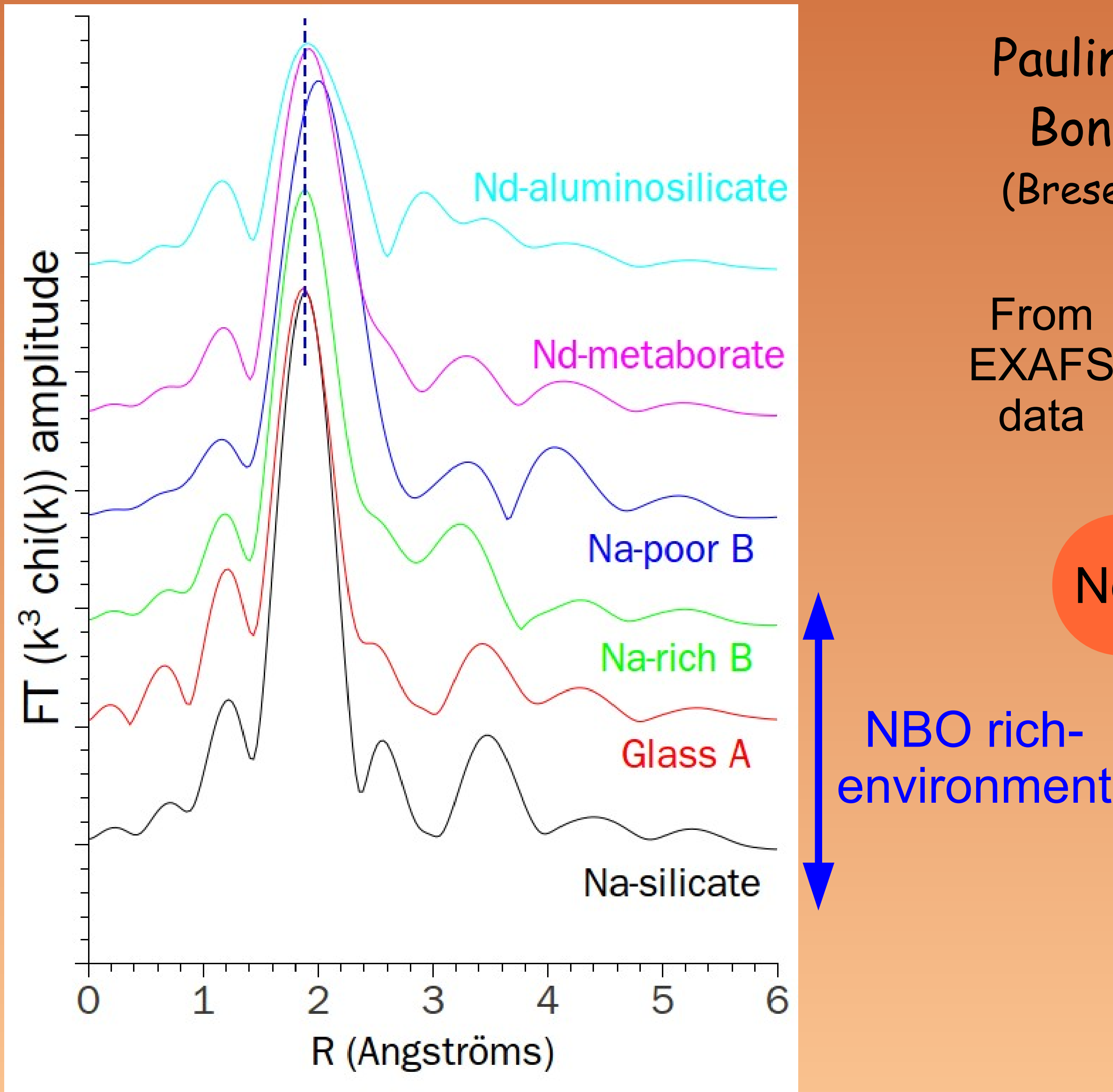

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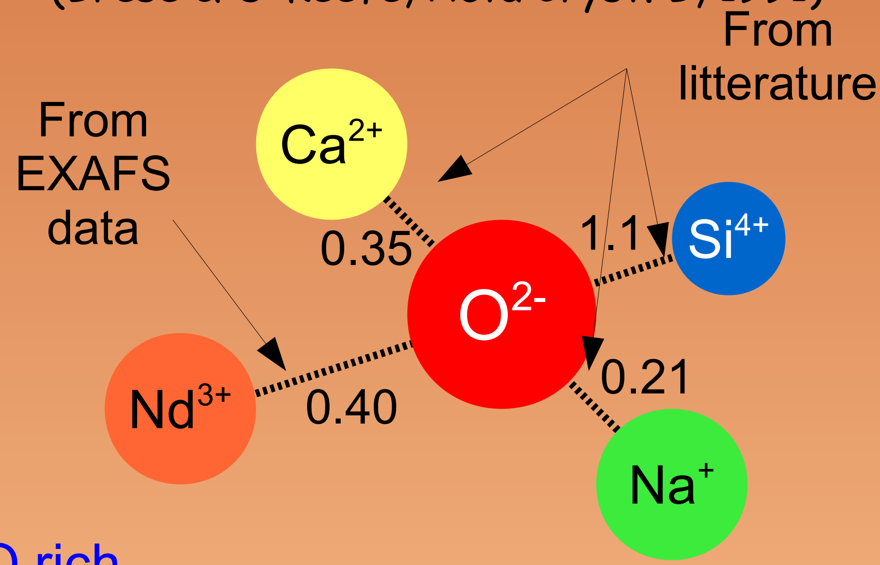

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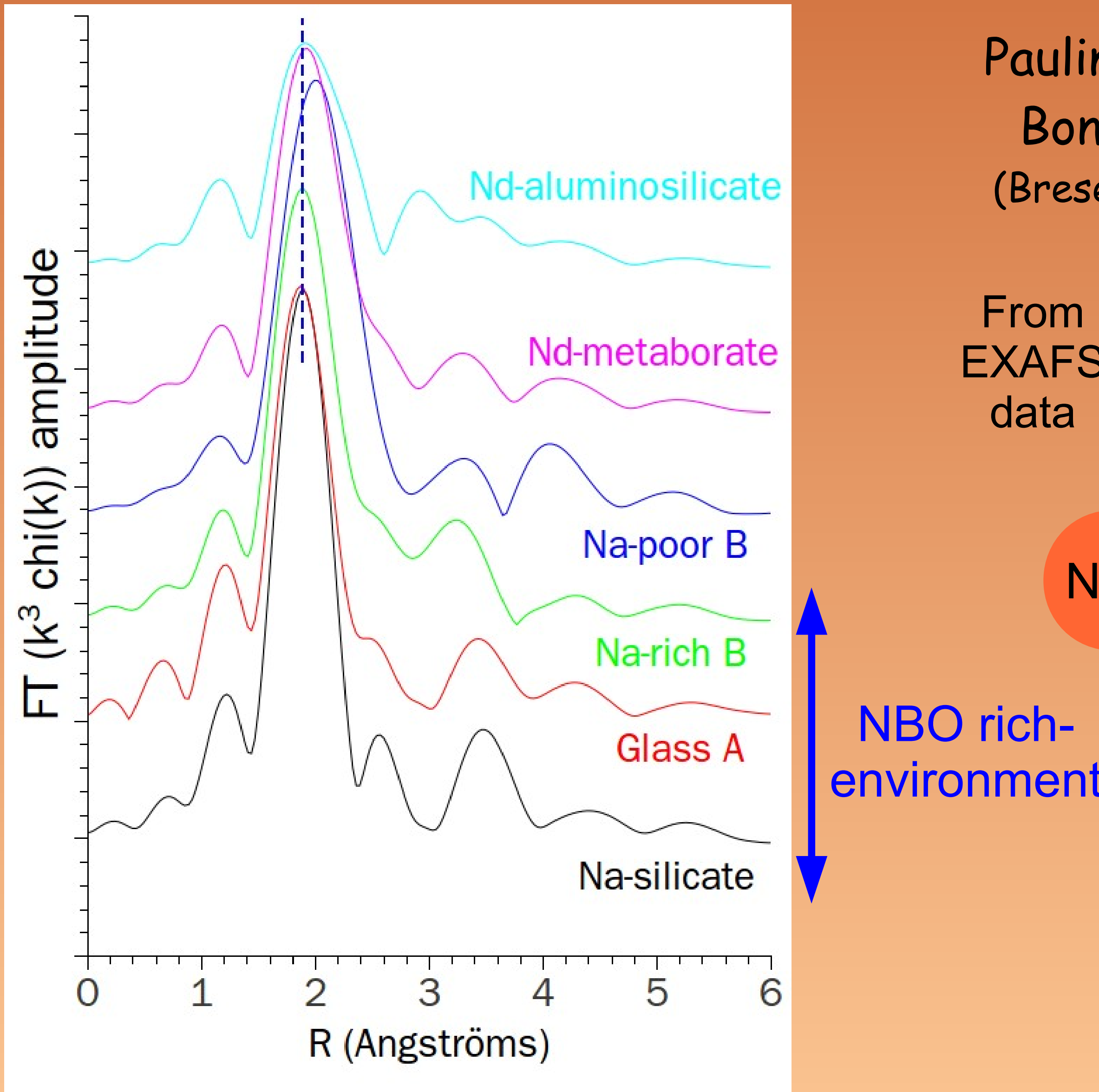

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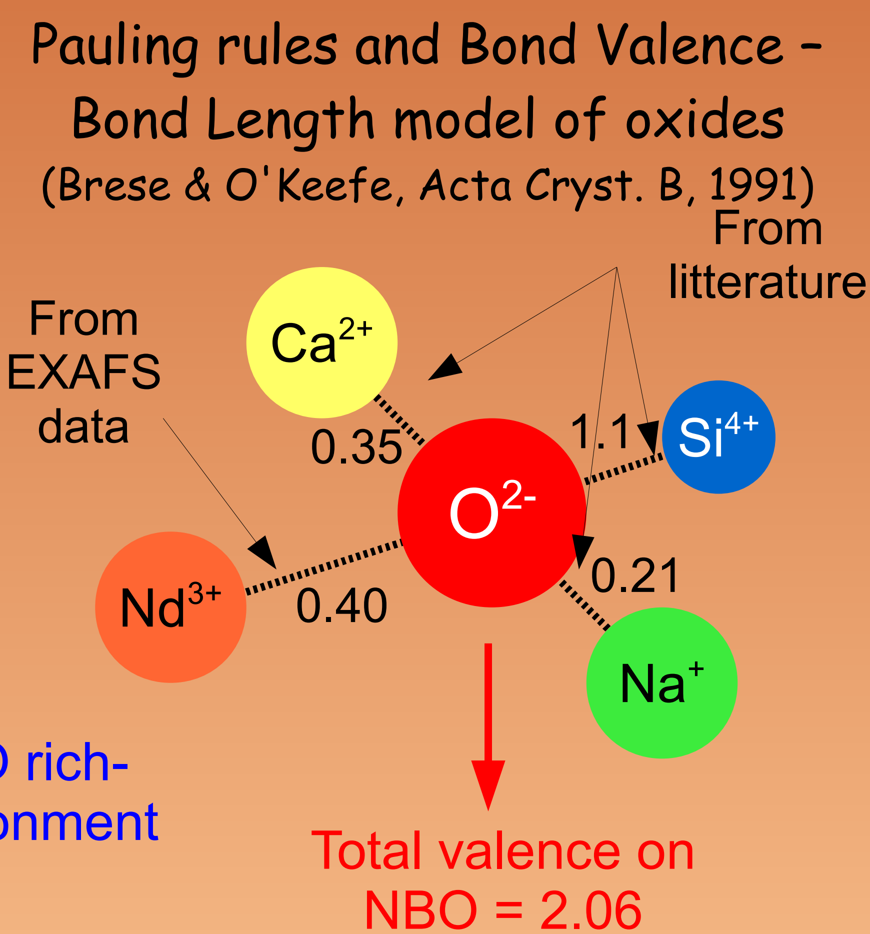

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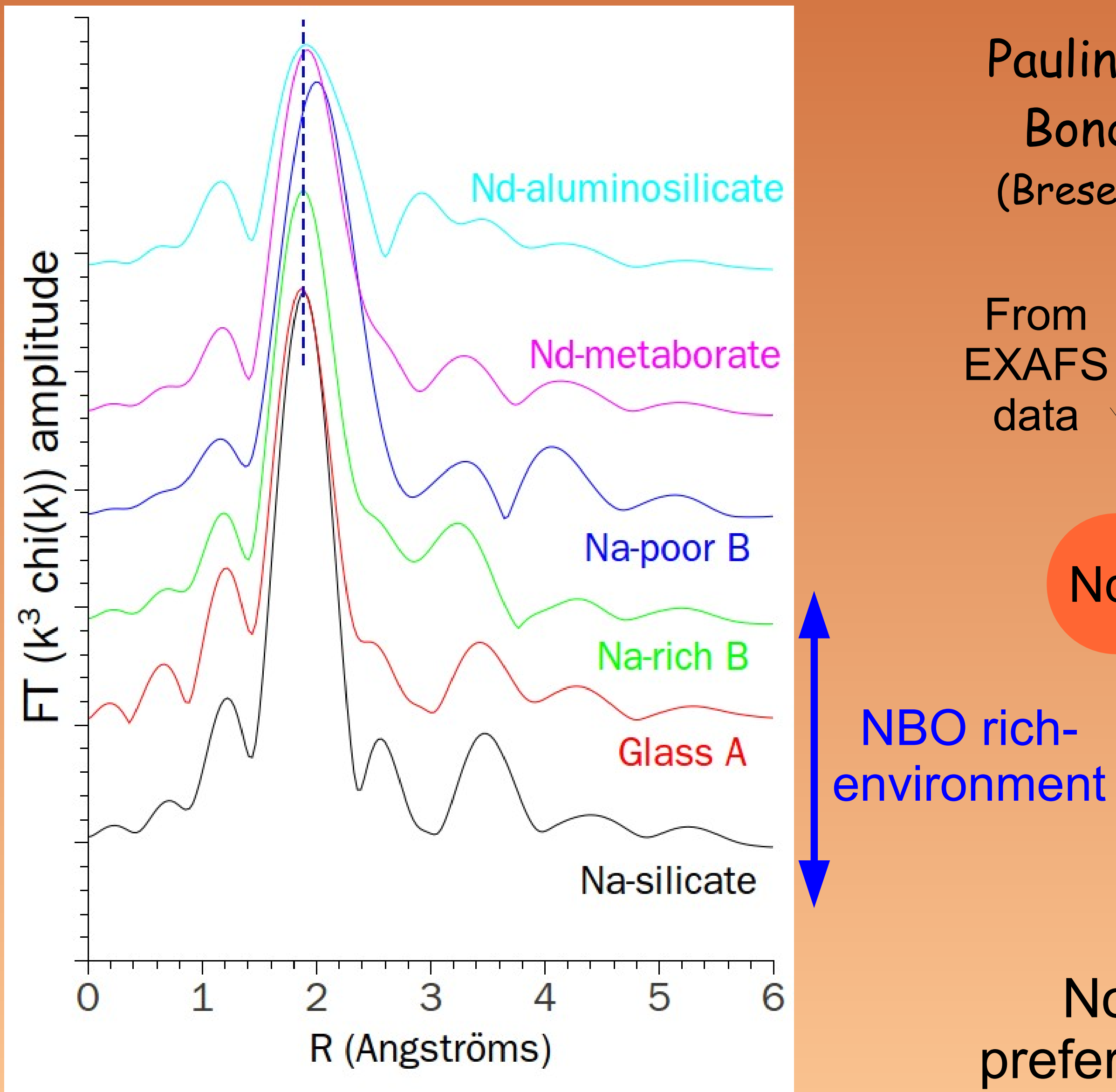

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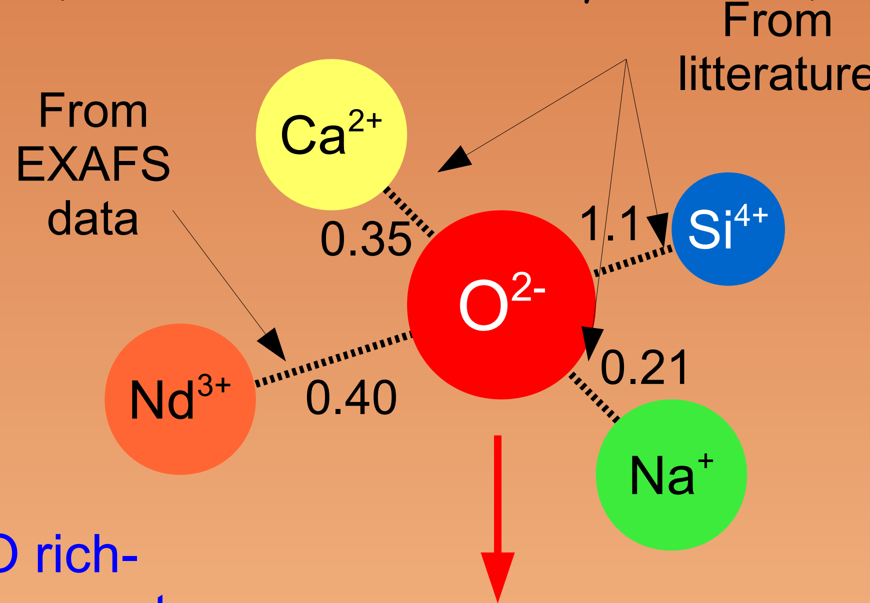
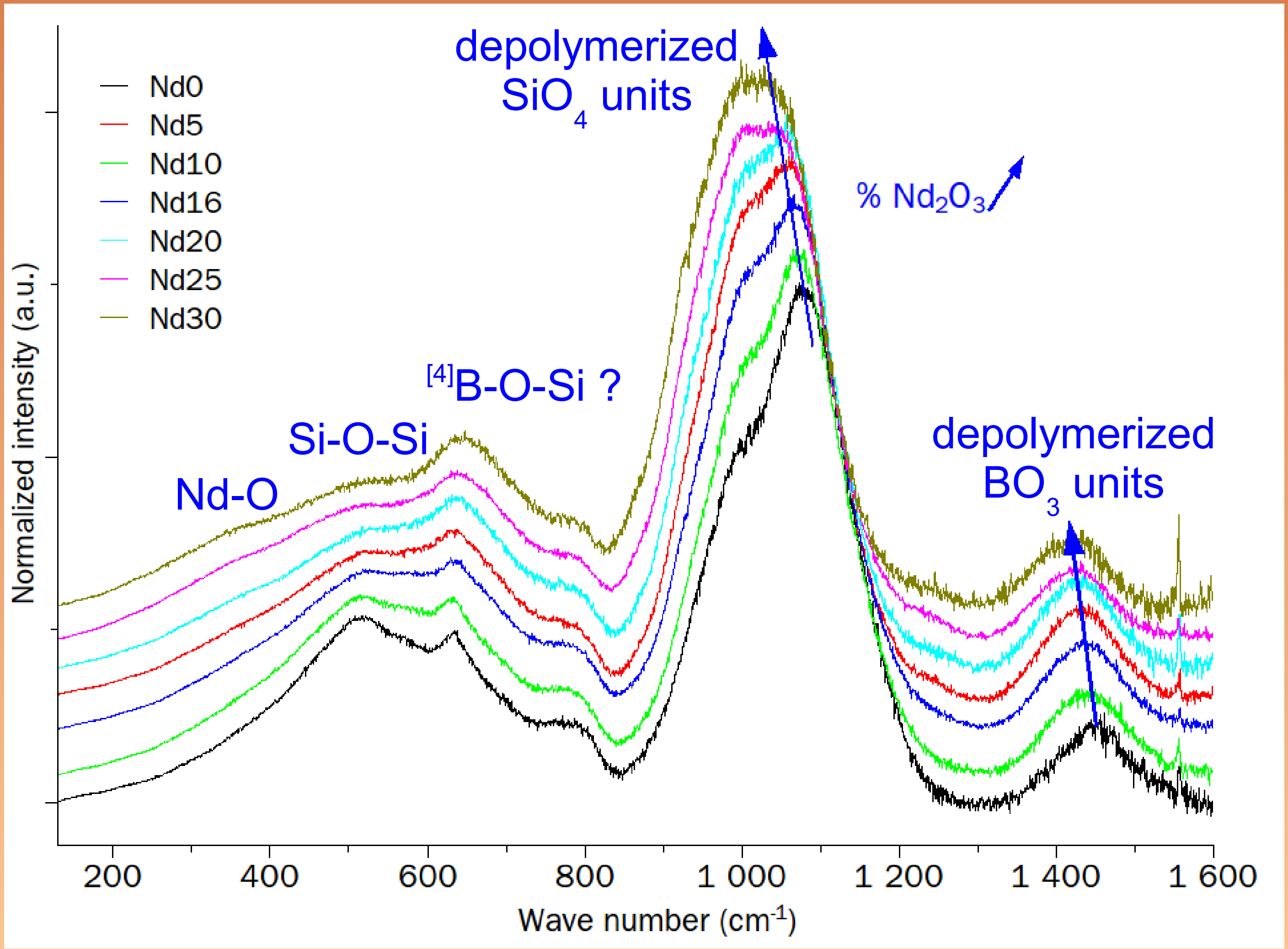


Total valence on NBO = 2.06

No evidence for Ca^{2+} or Na^{+} preferential charge compensation

Majérus et al., JNCS 2008

Effect of Nd_2O_3 content on the aluminoborosilicate network



With increasing % Nd_2O_3

Low-frequency shift of
- Depolymerized BO_3 band
- Q^3 band

B-O-Si band is affected

Raman spectra (λ_{exc} = 488 nm) on glass A series with 0 to 30 wt% Nd_2O_3

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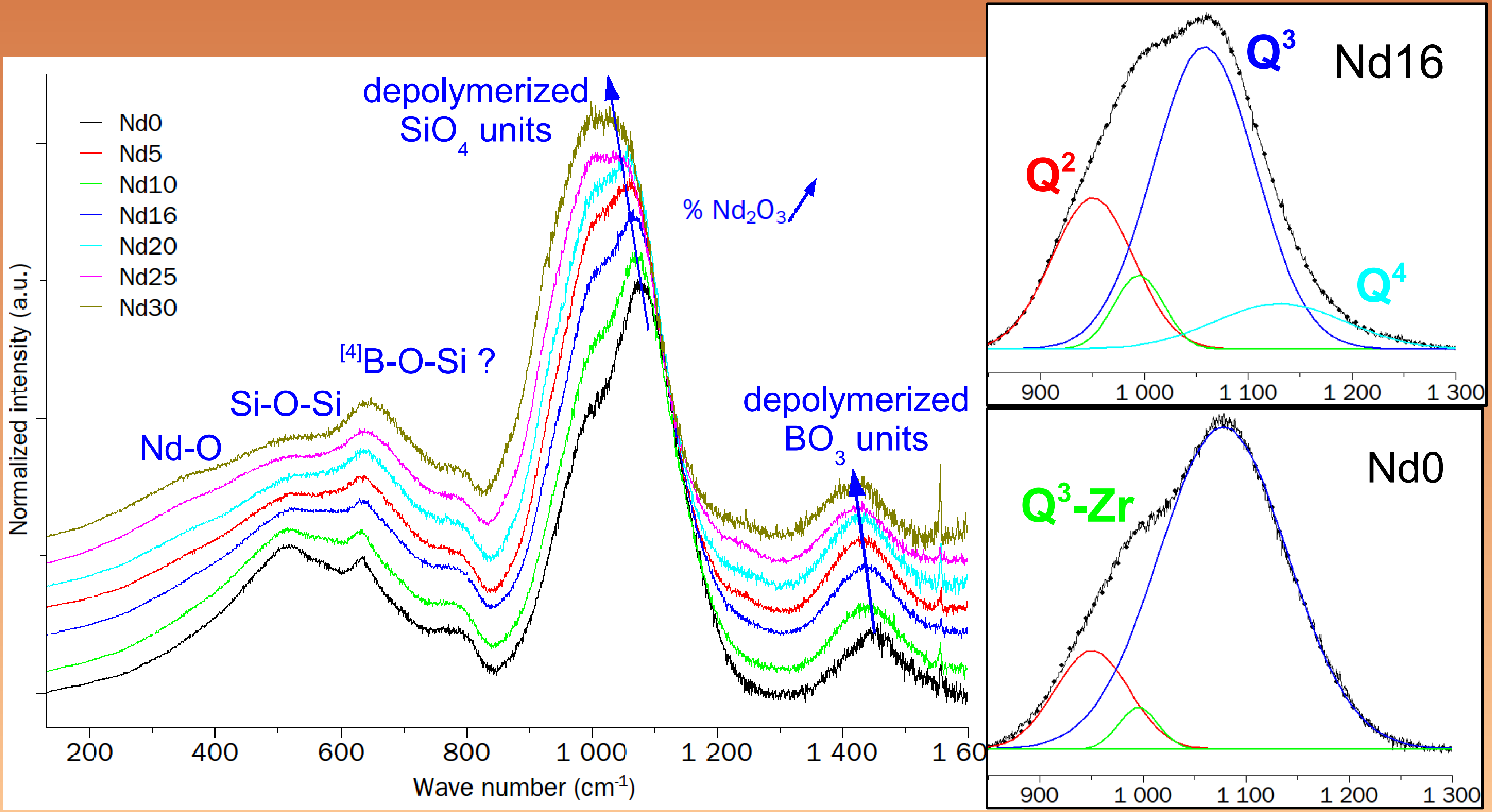

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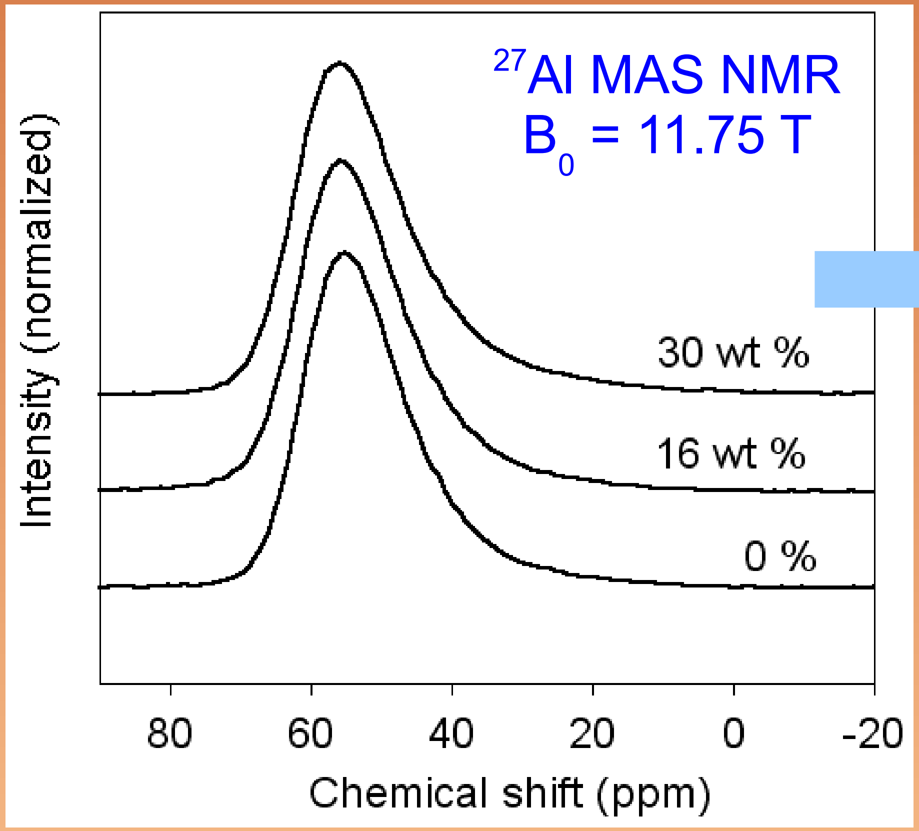
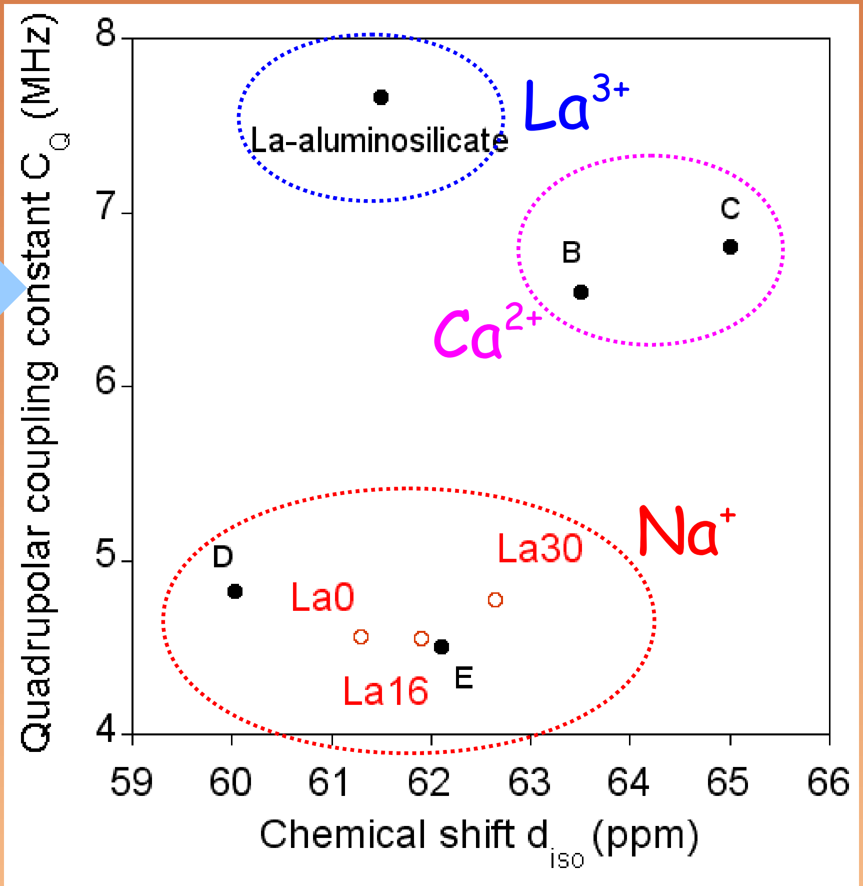
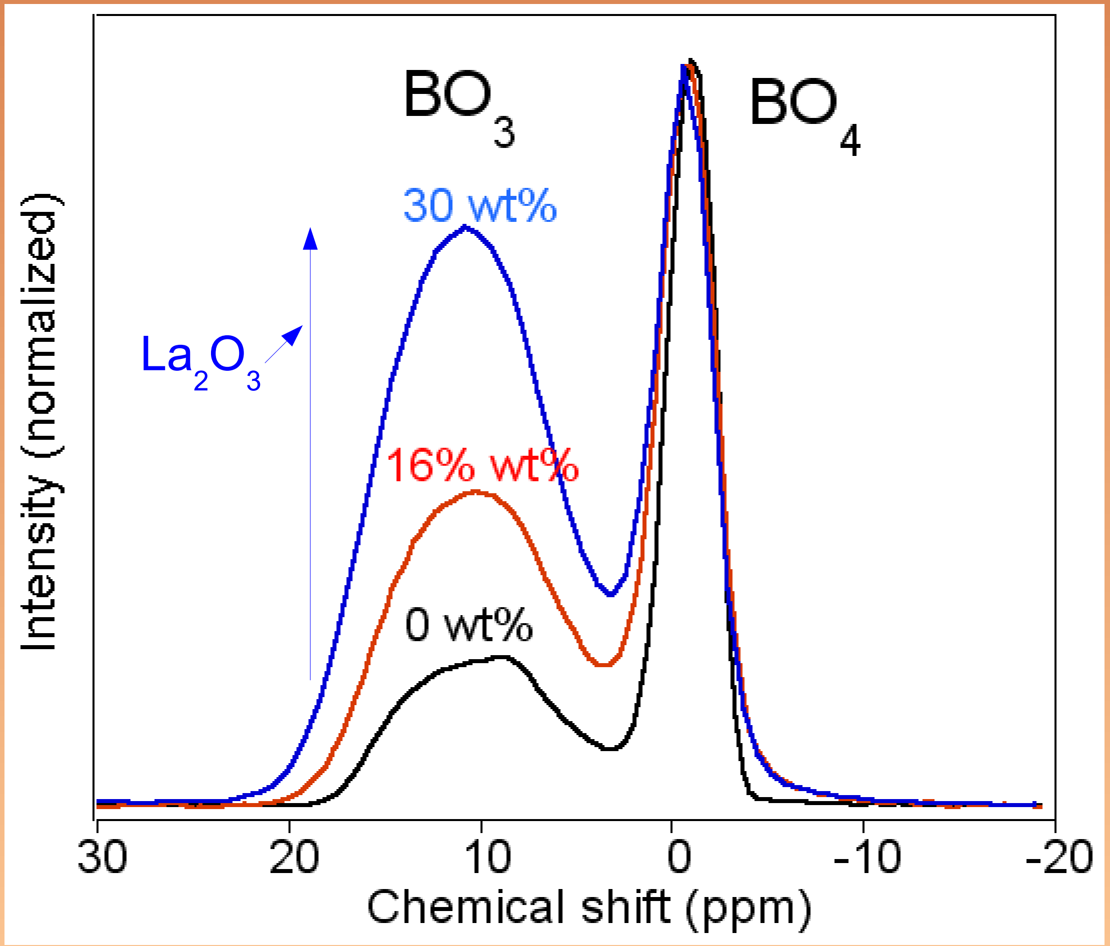




La_2O_3 incorporation has little effect on AlO_4 units, that are charge compensated by Na^+ ions

Effect of Nd_2O_3 content on the aluminoborosilicate network

^{11}B MAS NMR, B_0 = 11.75 T



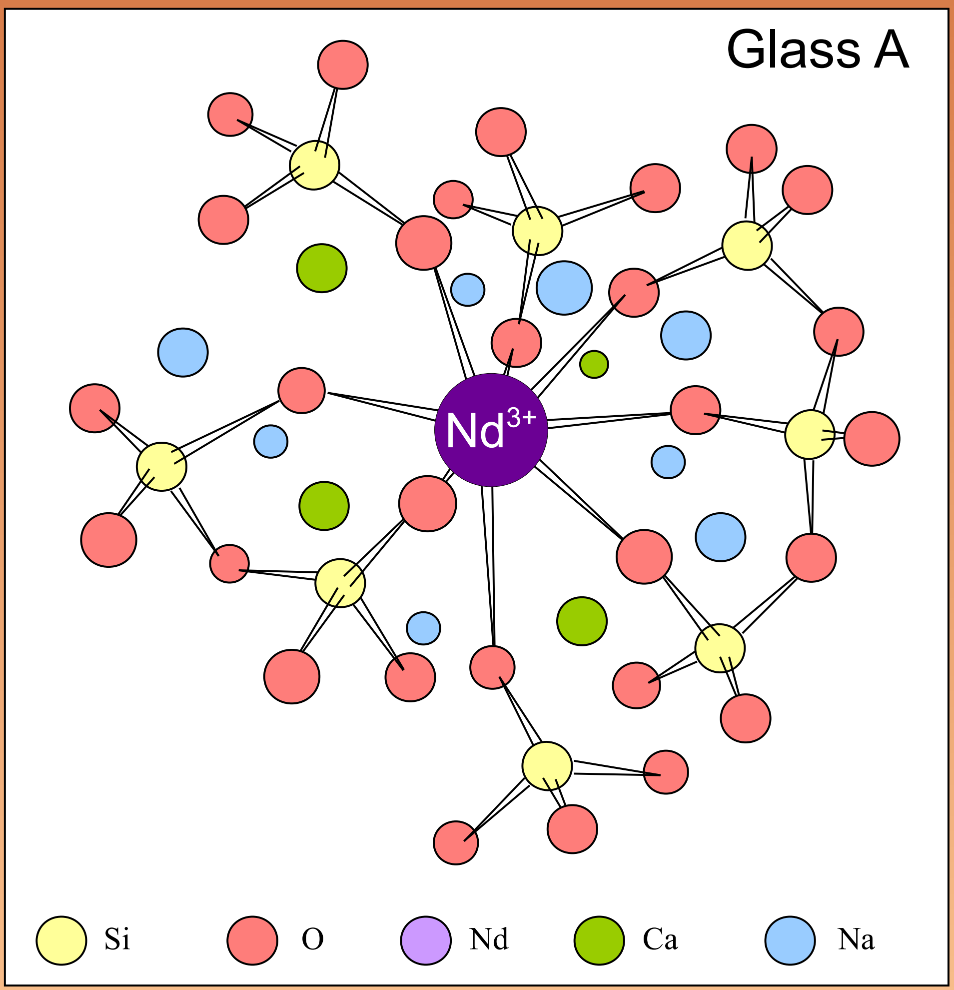
BO4 fraction ↘

60 %

42 %

30 %

Summary of Nd_2O_3 incorporation into the model glass



- Incorporation in depolymerized areas enriched in NBO/Na^+ and Ca^{2+}
- Depolymerization of the silicate network (creation of NBO), principally by formation of Q^2 units
- Destruction of BO_4 units as BO_3 + NBO
- No change of AlO_4 units

Consistent with the formation of the $Nd(O)_7$ coordination sphere

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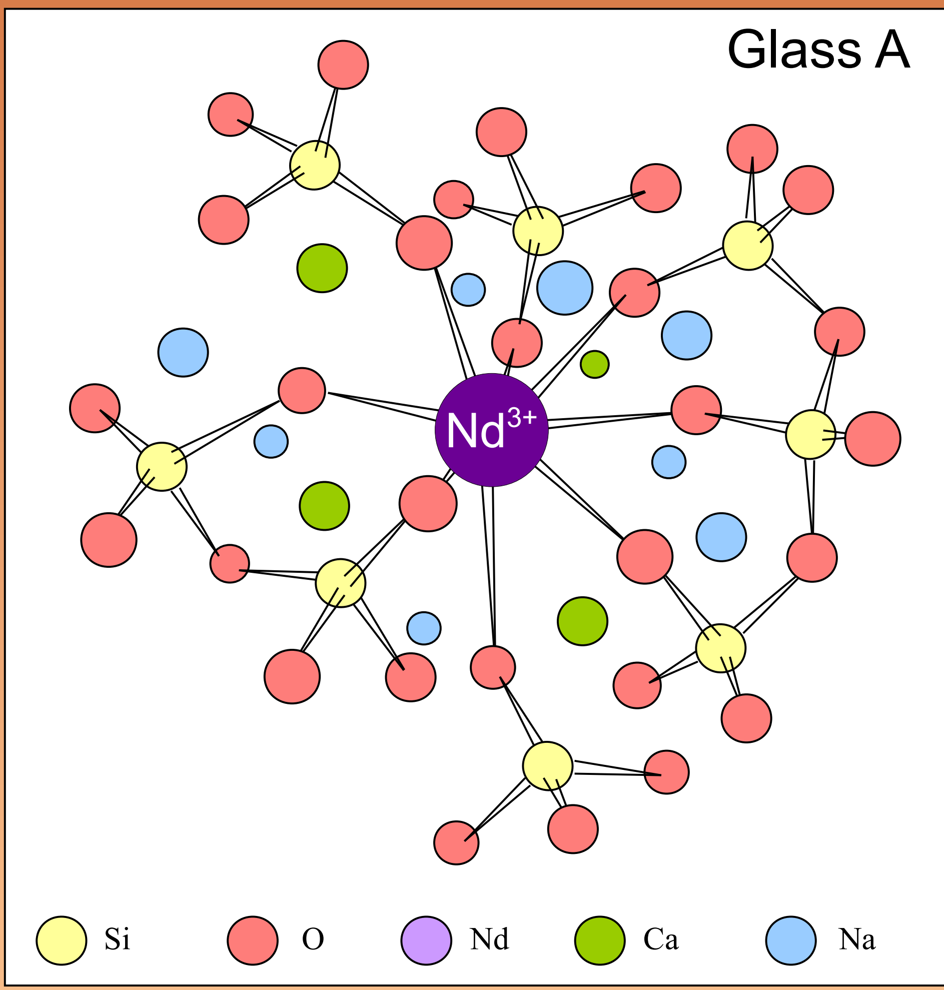

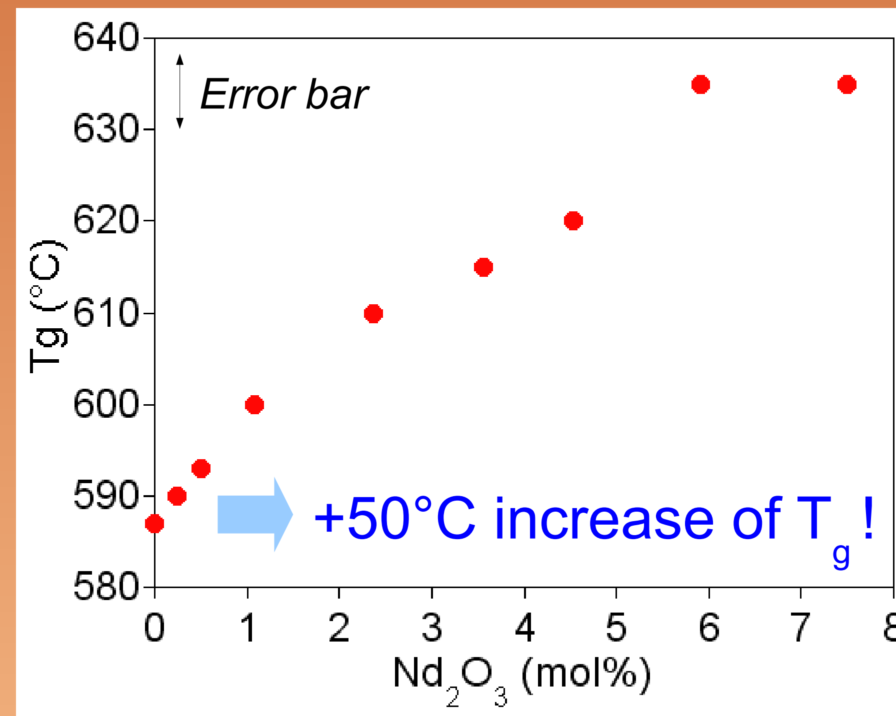

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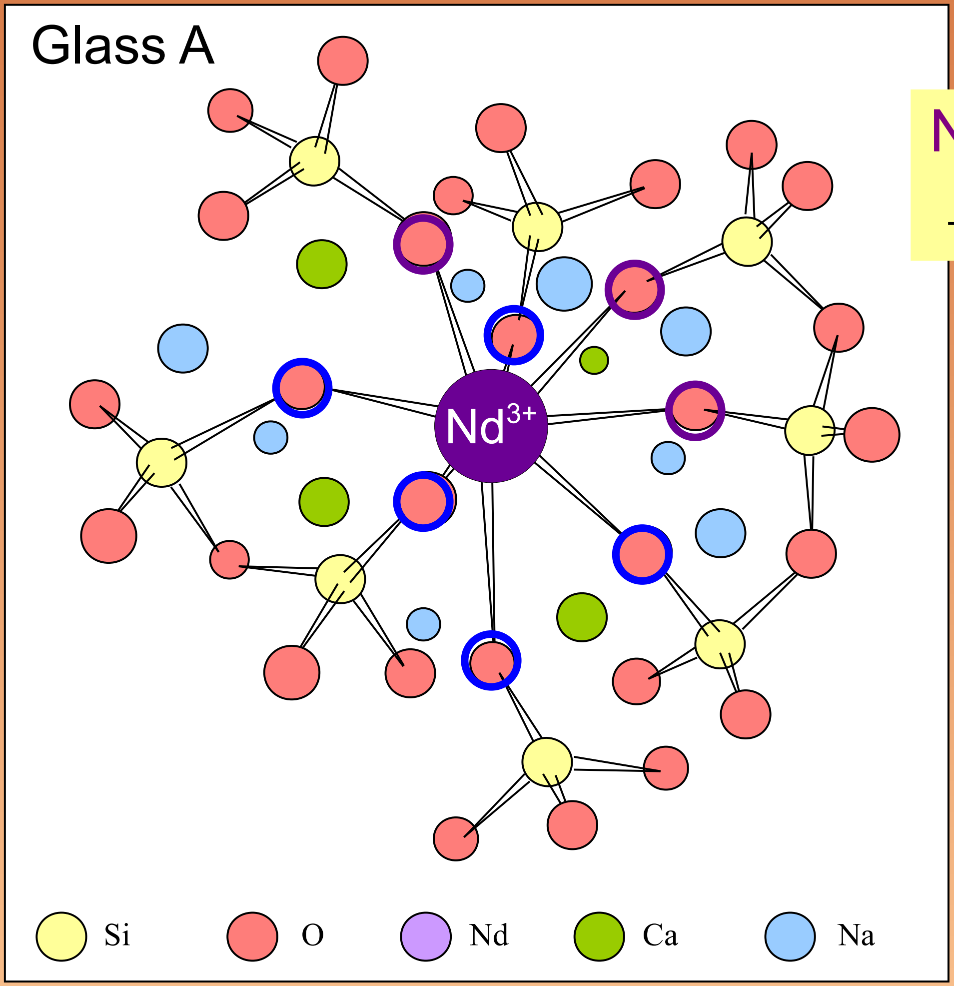
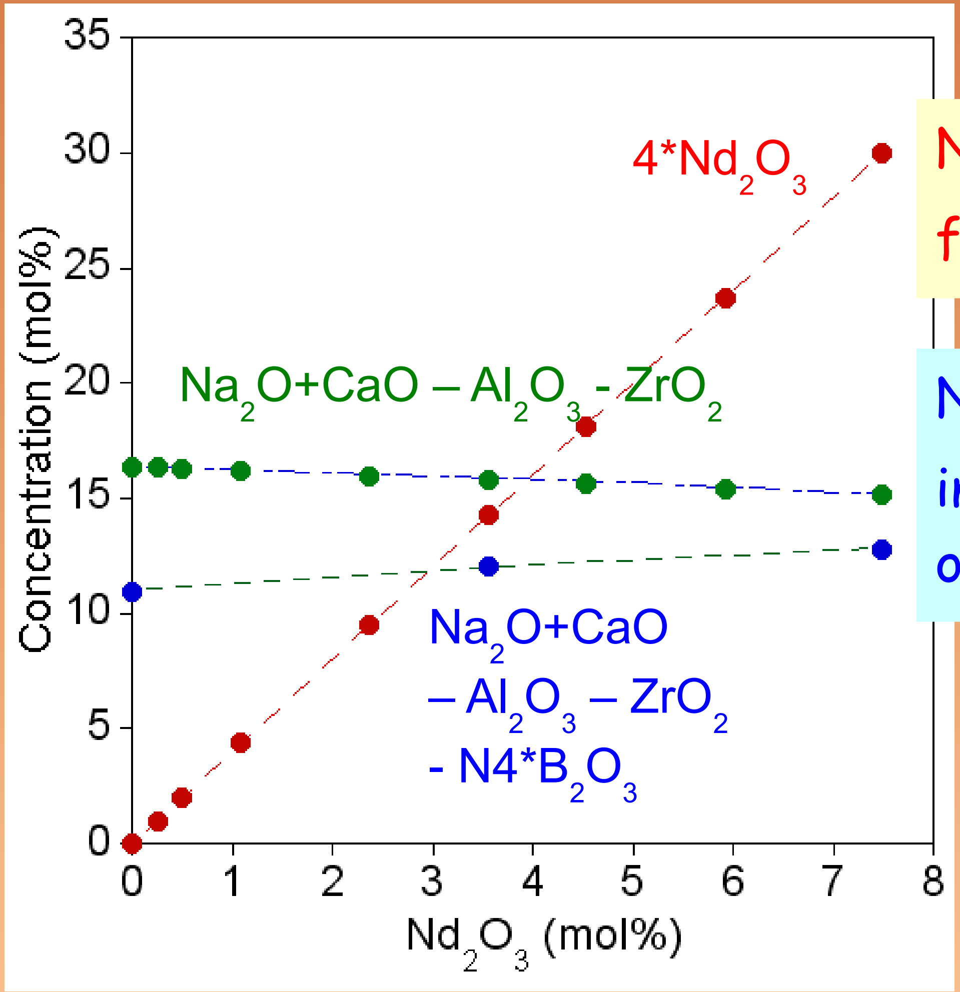


$Nd_2O_3 + 4\ Na_2O$
$\rightarrow 2\ (Nd^{3+} + 3\ NBO + 4\ NBO) + 8\ Na^+$

$Nd(O)_7^{4-}$

4 moles of Na_2O/CaO are necessary to incoporate 1 mole Nd_2O_3

Availability of charge compensating cations as a function of Nd_2O_3 content



Number of Na_2O + CaO necessary to form the $Nd(O)_7$ coordination sphere

Number of Na_2O + CaO avalaible taking into account the charge compensation of $(AlO_4)^-$, $(ZrO_6)^{2-}$ and $(BO_4)^-$ units

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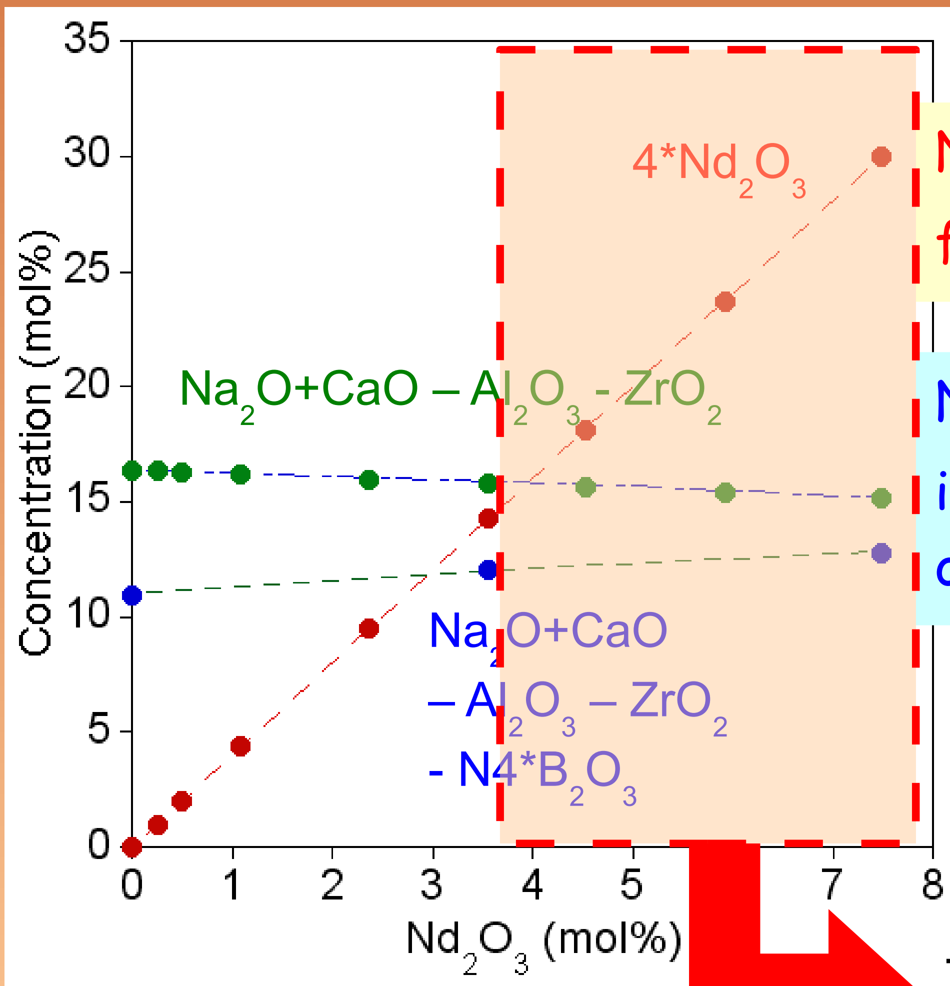

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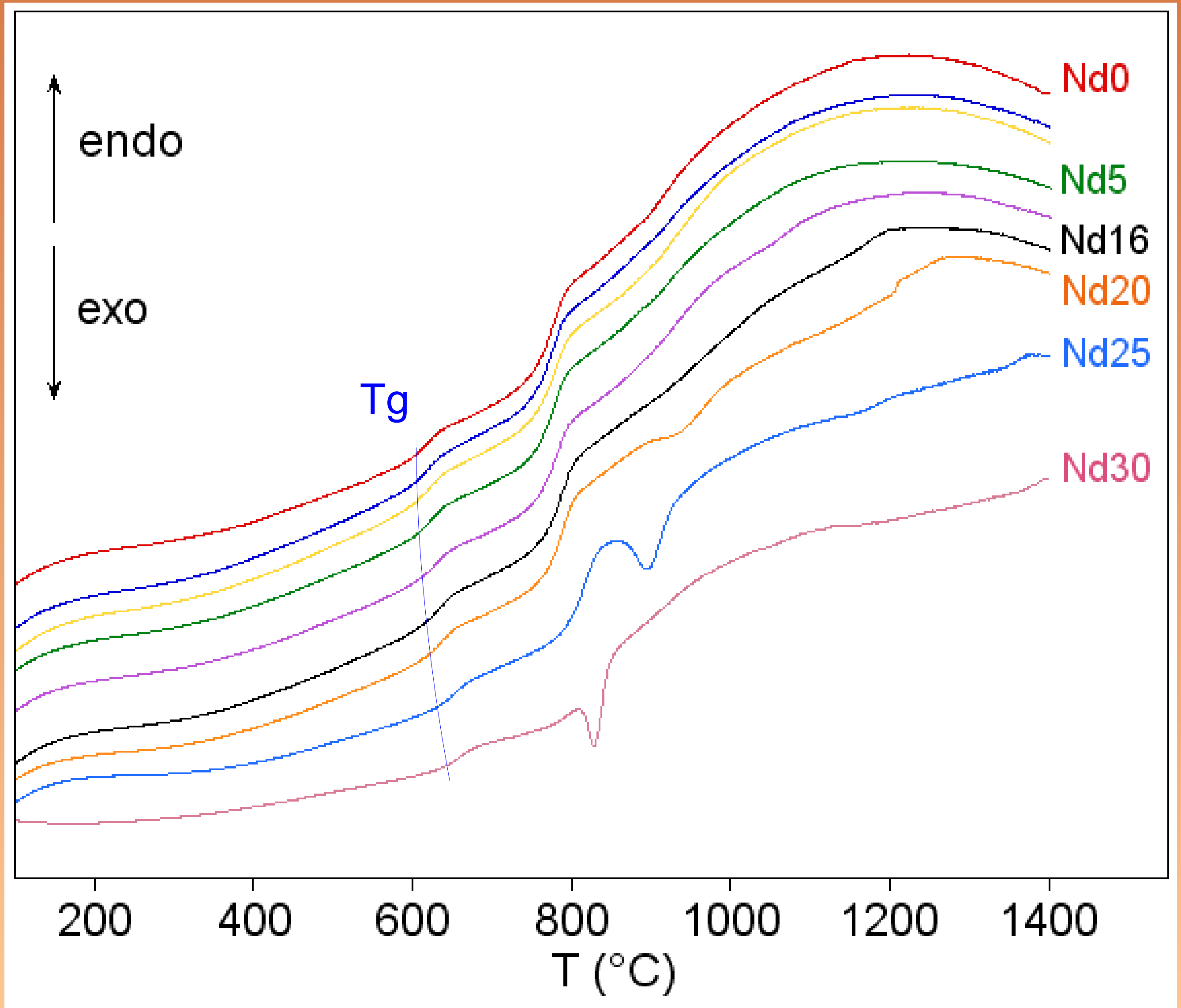
On this range Nd^{3+} ions can not find enough NBO to incorporate as isolated $Nd(O)_7$

Crystallization study

DTA at 10°C/min of glass powder, 80-125 µm



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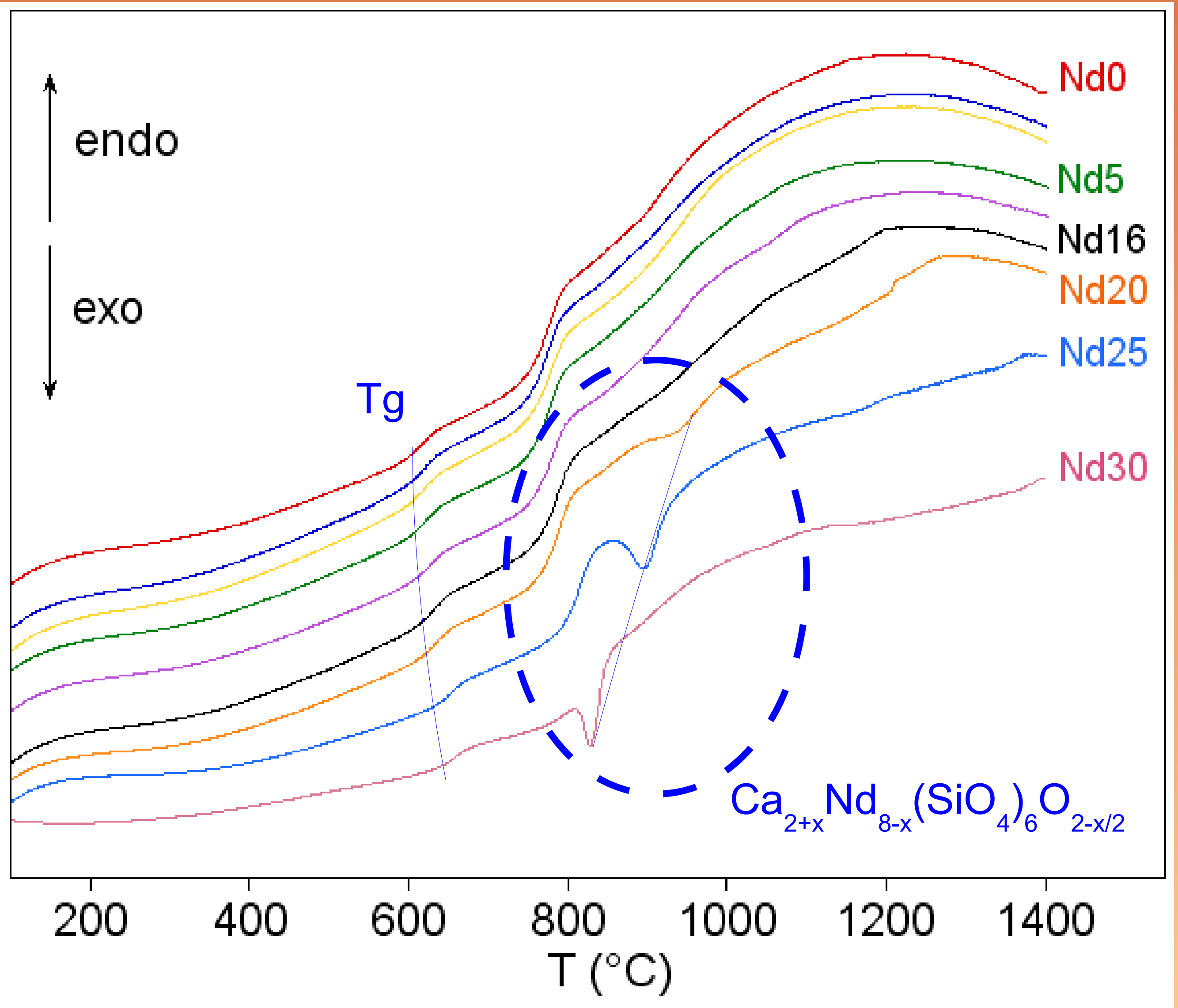
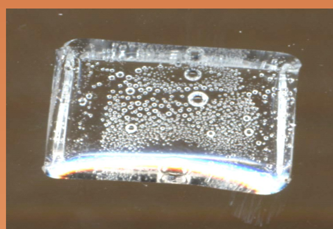


Crystallization of a Nd-silicate apatite beyond 4 mol% - 16 wt% Nd_2O_3

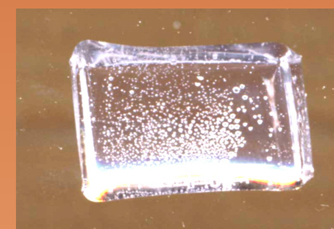
Crystallization study

Slow cooling from the melt at 6°C/min

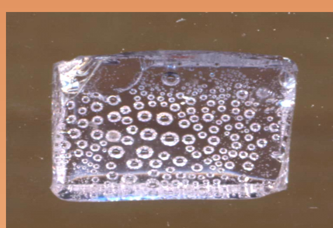


Nd0

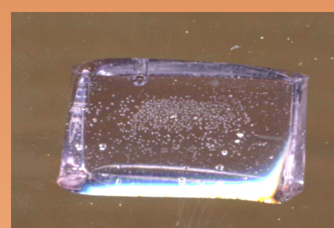
Nd1,3



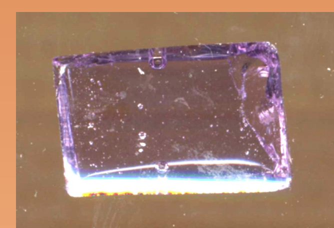
Nd2,5



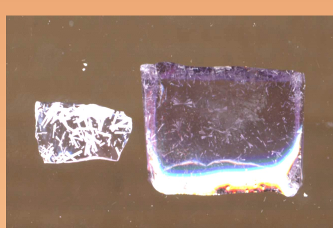
Nd5



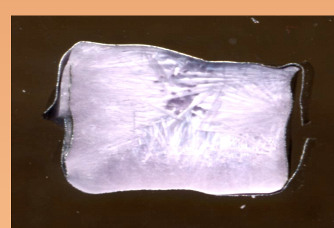
Nd10



Nd16



Nd20



Nd25

Nd30

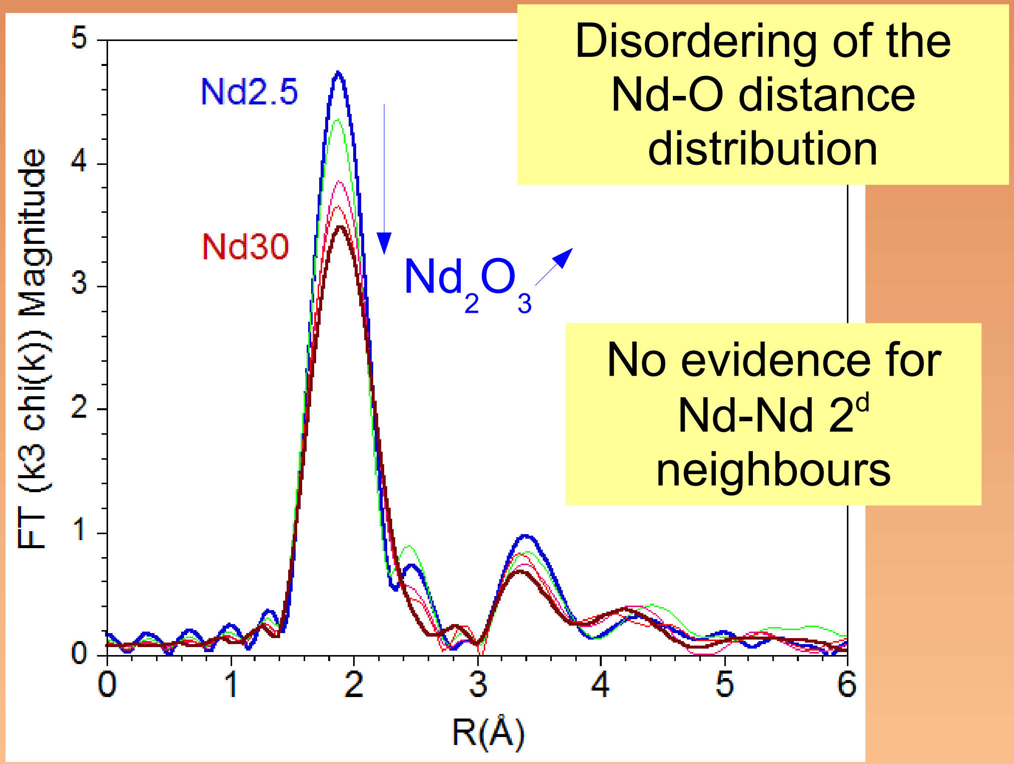
Crystallization of a Nd-silicate apatite beyond 4 mol% - 16 wt% Nd_2O_3

Summary and composition changes

Beyond 4 mol% (16 wt%) Nd_2O_3, Nd^{3+} ions :

- Are bonded to NBO's and to BO's
- And/or share their NBO's through clustering in the glass structure

No conclusive evidence from EXAFS and optical absorption spectra. Nd^{3+} luminescence decay study is under way.



Nd L_3-edge EXAFS at 77 K

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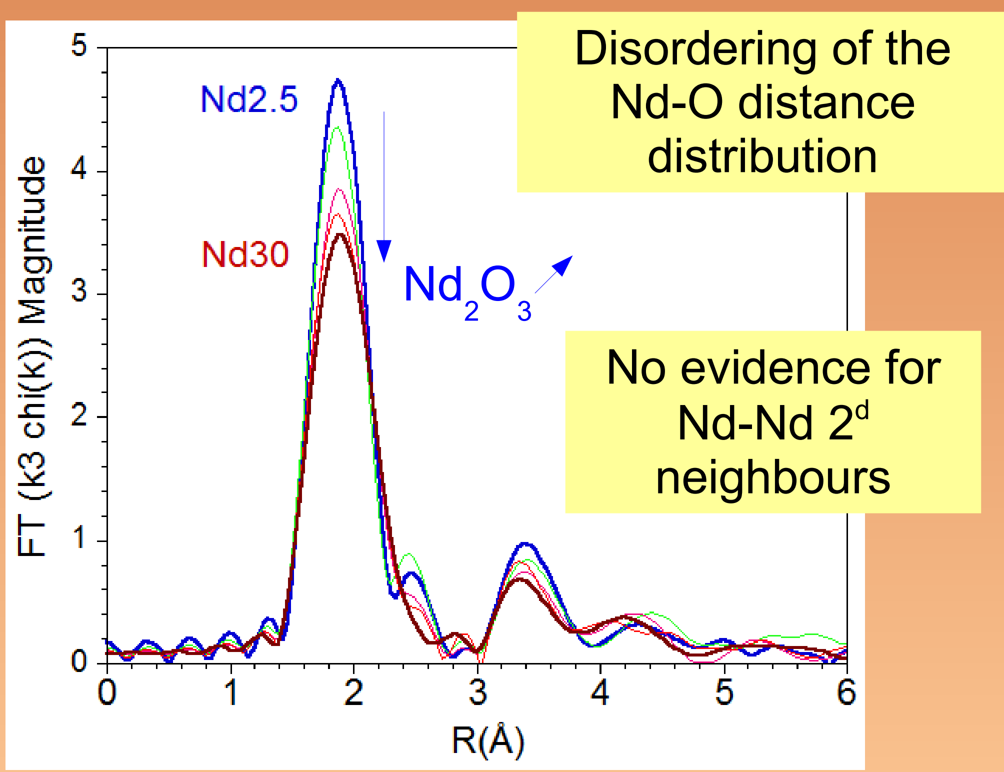

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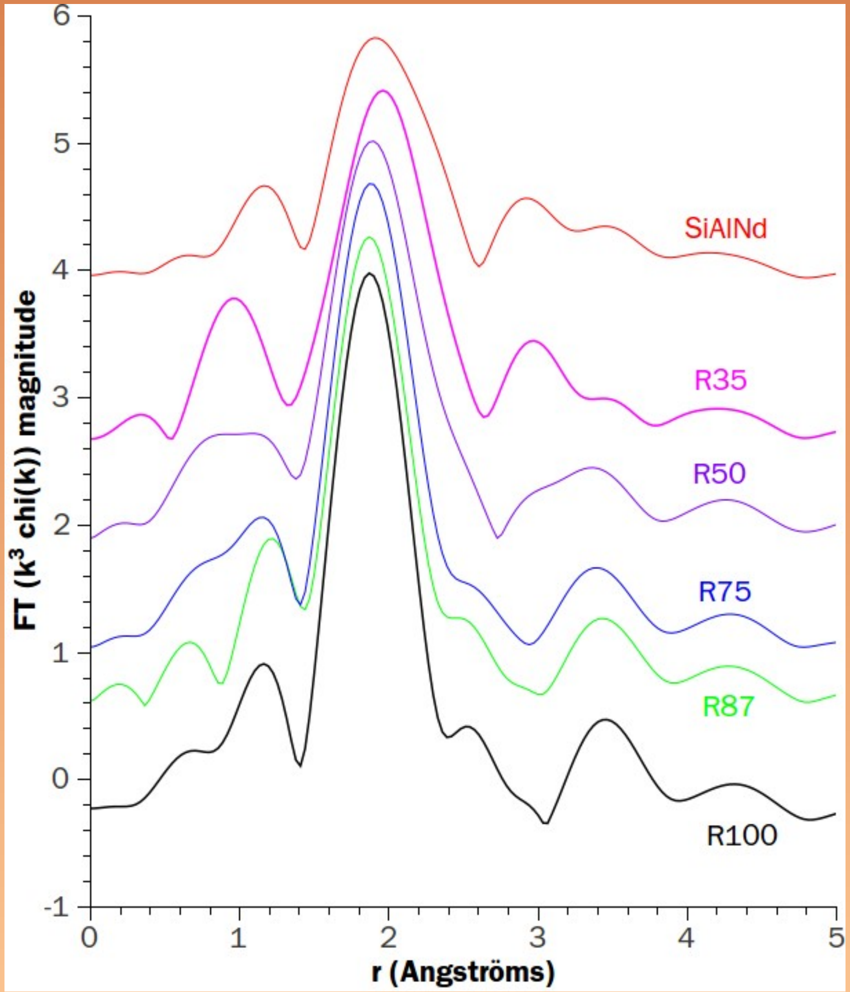
Relationship between this composition threshold and the crystallization of Nd-silicate apatite

What happens when CaO and Na_2O are lacking

- In Al_2O_3 enriched glass ?
- *In B_2O_3 enriched glass ?*

O. Majérus et al., JNCS. 357 (2011) 2744-2751

Nd^{3+} in peraluminous glasses



$$R = \frac{Na_2O + CaO}{Na_2O + CaO + Al_2O_3}$$

A glasses with R varying from 1 to 0.35 (15.4 mol% Al_2O_3)

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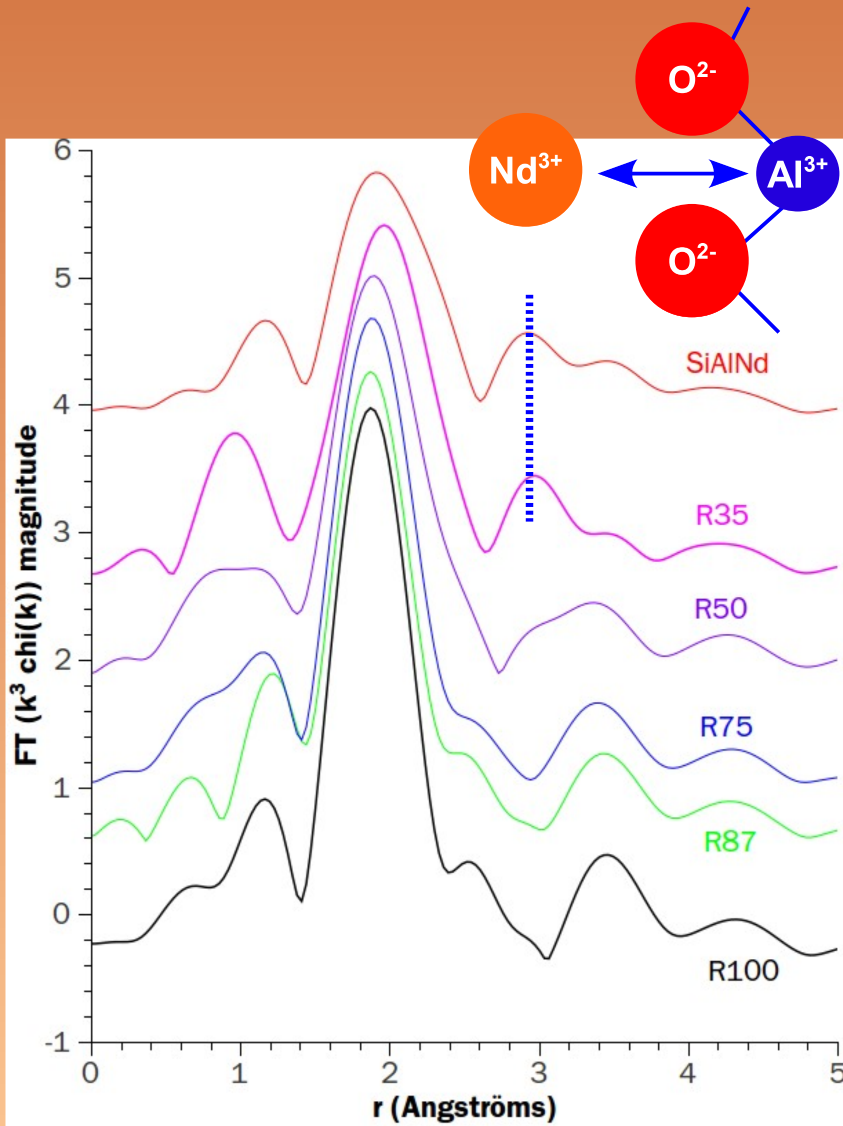

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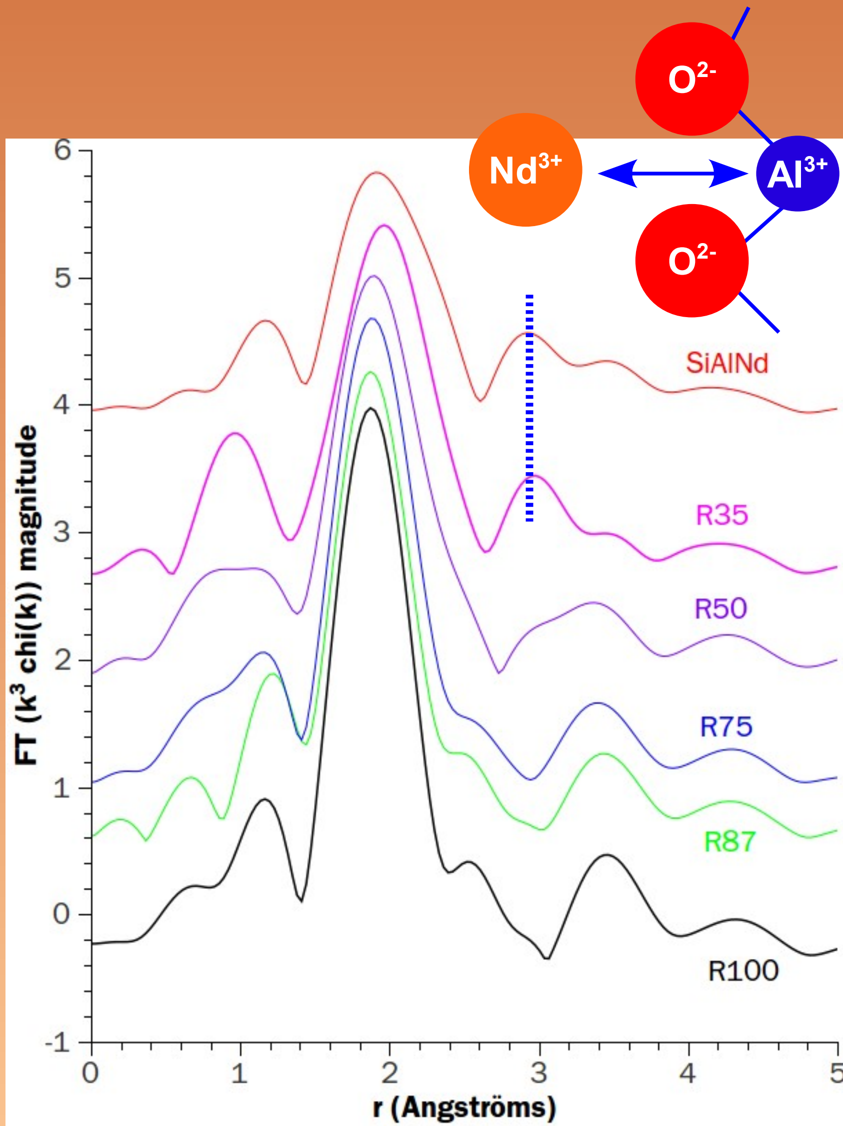

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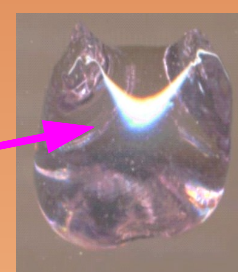
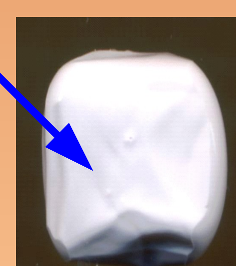


When R < 0.5
Nd^{3+} become charge compensators of $(AlO_4)^-$ units
Confirmed by ^{27}Al MAS NMR



Nd^{3+} solubilization in the glass

Slow cooling from the melt at 6°C/min

Conclusions

Model glass A (mol%) :

SiO_2	Al_2O_3	B_2O_3	Na_2O	CaO	ZrO_2	Nd_2O_3
61.8	3.0	9.0	14.4	6.3	1.9	3.6

- A well-defined 6-8 O coordination sphere is inferred from the Nd^{3+} spectroscopic data (optical spectroscopy and EXAFS)
- Compensation of the excess negative charge of the $Nd(O)_7$ complex is provided by Na^+ and Ca^{2+} ions. Good agreement of the mean Nd-O distance and the BV-BL calculations considering the $Nd(O)_7$ model
- Nd_2O_3 incorporate within the depolymerized areas and create NBO's mostly as Q^2 units
- There is an obvious relationship between the composition threshold where modifier oxides are « lacking » to form the $Nd(O)_7$ complex and the crystallization of Nd-silicate apatite
- Nd^{3+} ions can play different structural roles in the aluminoborosilicate system with very different compositions to that of glass A (peraluminous, LaBS glasses, etc)

Thank you for your kind attention !

Many thanks to HASYLAB staff (Germany), Rita Baddour and J-P. Pereira-Ramos (ICMPE, CNRS Thiais)

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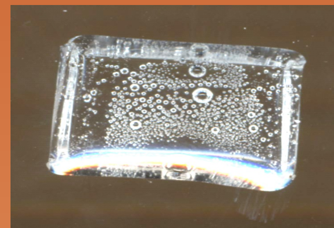
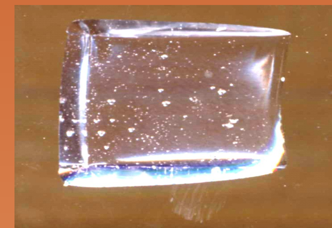
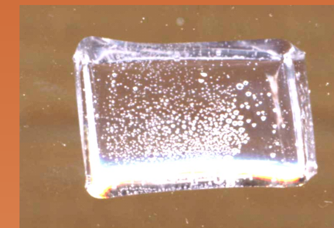


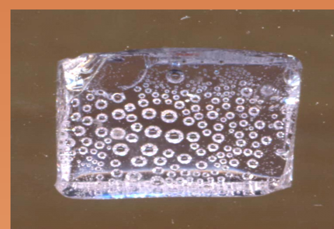
Nd0



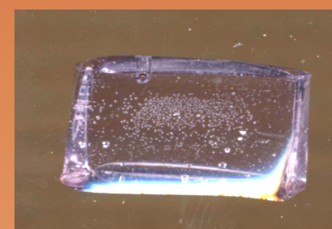
Nd1,3



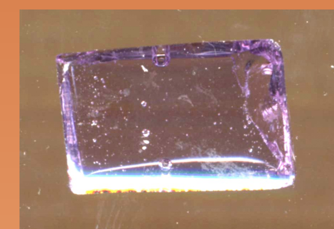
Nd2,5



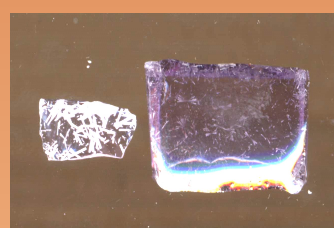
Nd5



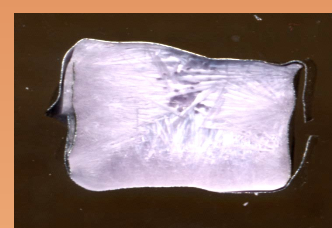
Nd10



Nd16



Nd20



Nd25

Nd30