

# Ce/Al correlation in aluminosilicate glasses and optical silica fiber preforms

*In press*

*10.1016/j.jnoncrysol.2017.08.035*

**M. Rita Cicconi<sup>1</sup>**, Dominique de Ligny<sup>1</sup>, Alexander Veber<sup>1</sup>,  
Wilfried Blanc<sup>2</sup>, François Baudelet<sup>3</sup>, Daniel R. Neuville<sup>4</sup>

1 - Department Werkstoffwissenschaften, Lehrstuhl für Glas und Keramik, Universität Erlangen-Nürnberg, Germany

2 - Université Côte d'Azur, CNRS, Institut de Physique de Nice, UMR 7010, France

3 - Synchrotron SOLEIL, F-91192 Gif s/Yvette, France

4 - Institut de Physique du Globe de Paris, CNRS, F- 75238 Paris, France



Yb or Tm-based glass fibers -> Al-Ce codoping has been studied as an effective way to reduce photodarkening (PD)<sup>#</sup>

Actual explanation ->  $\text{Ce}^{3+} / \text{Ce}^{4+}$  -> provides means for trapping both hole- and electron-related color centers



---

Explain the photodarkening attenuation in **SiO<sub>2</sub> glass fibers** Ce-Al codoped

- understanding the **role** of Al
- **quantifying** Ce redox ratios
- **quantifying** the Ce/Al correlation
- effect of the **atmosphere** during collapse of the preform
- link the glass **Optical basicity** to the Ce redox ratio in glasses

Explain the photodarkening attenuation in  $\text{SiO}_2$  glass fibers Ce-Al codoped

- understanding the **role** of Al
- **quantifying** Ce redox ratios
- **quantifying** the Ce/Al correlation
- effect of the **atmosphere** during collapse of the preform
- link the glass Optical basicity to the Ce redox ratio in glasses

## Difficulties due to the preform

Very high temperatures

Very low concentrations codopants

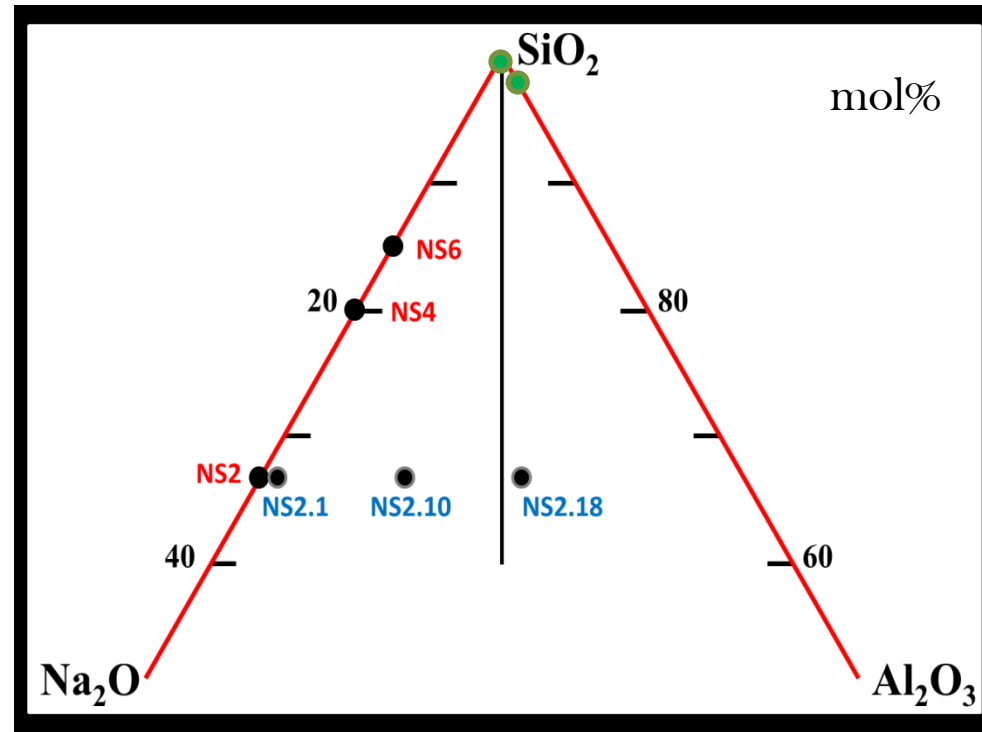
Al in higher coordination states [5] or [6]

Heterogeneous Al concentrations (solution doping technique)

-Synthesis of Na-aluminosilicate glasses doped with  $\text{CeO}_2$  (0.36 or 1.8 mol%)

- Ce-activated fiber preforms

Chemical vapor deposition (MCVD) method



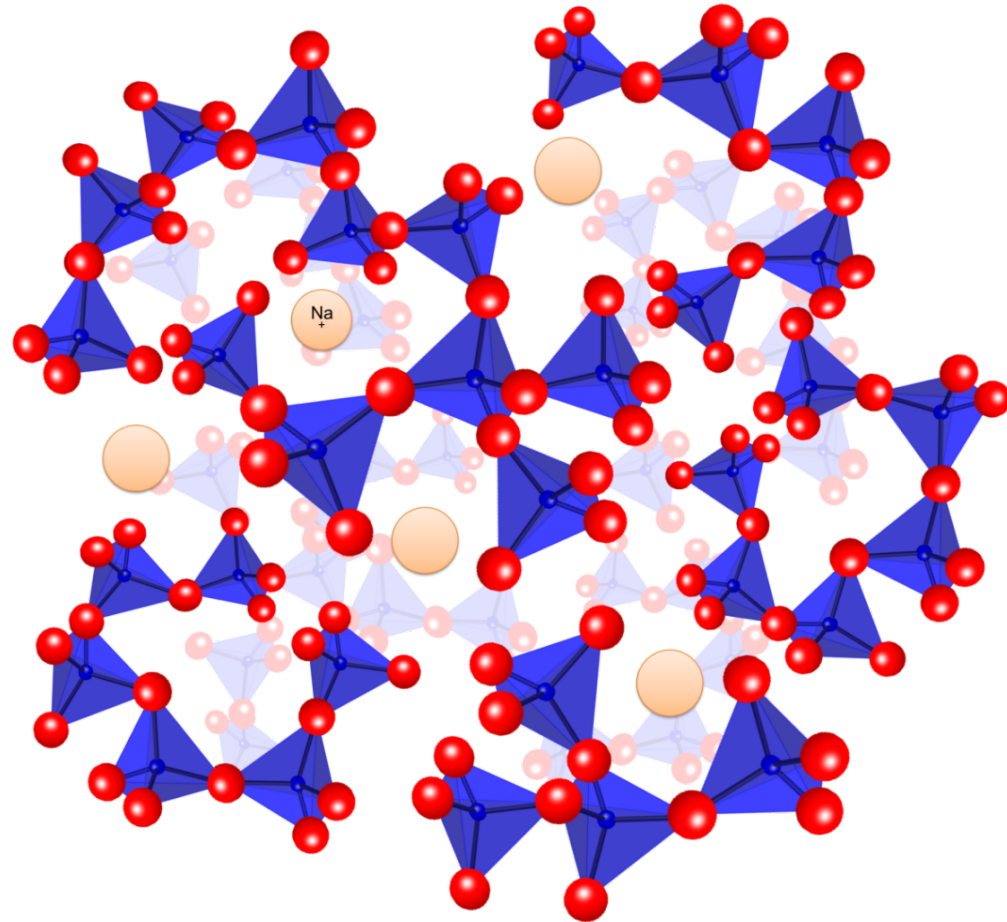
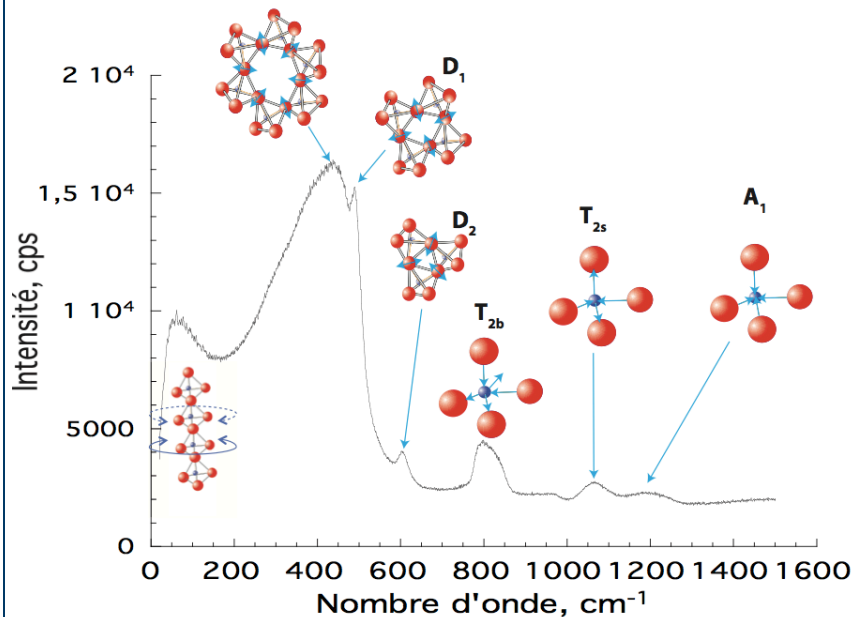
- Modifications of the glass structure -> Raman
- Ce redox ratio  $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$  -> XAS
- Optical properties depending on glass polymerization and Ce redox ratio



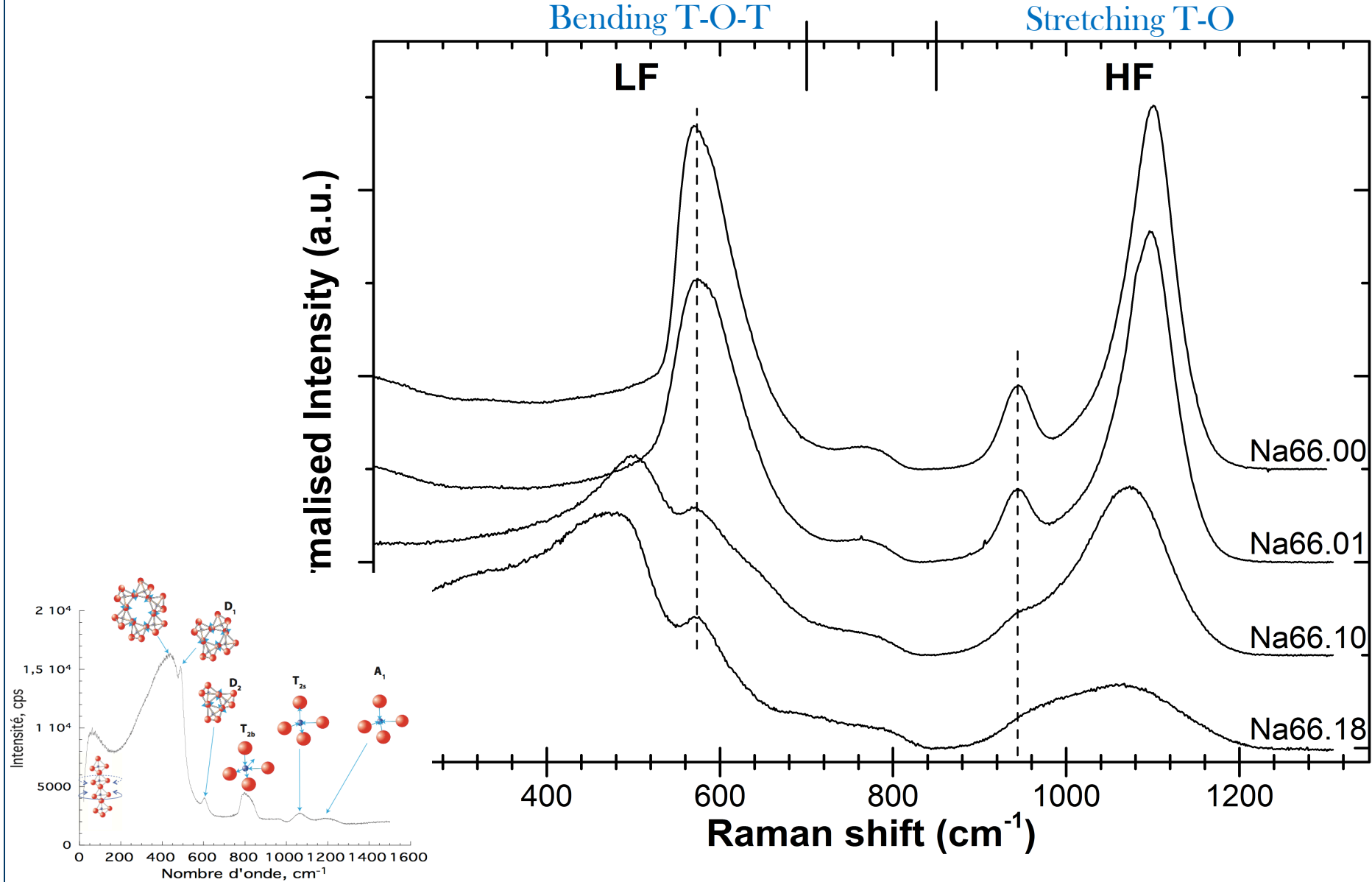
## Raman study of NA66.y glasses

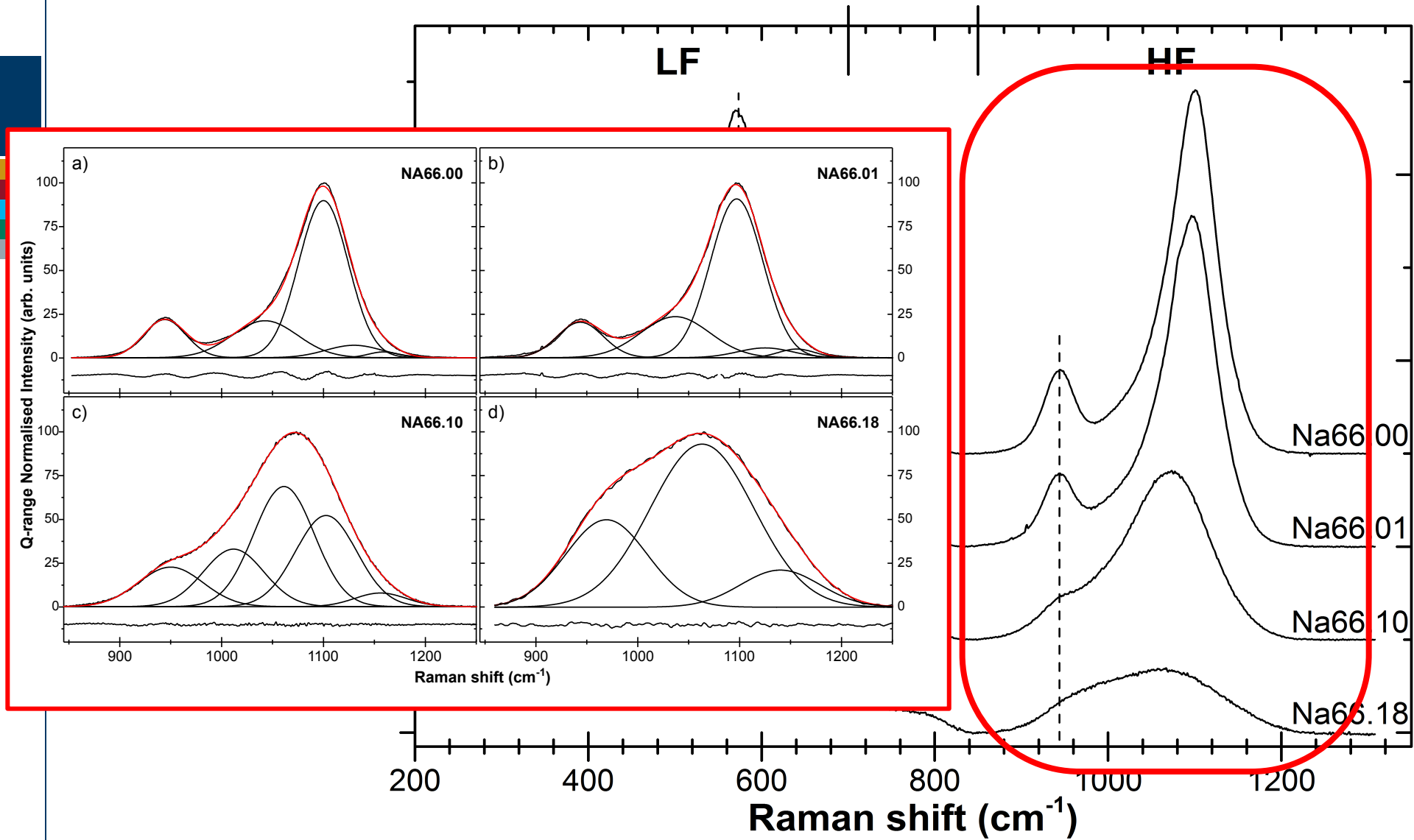
Adding Al Na is mobilised as charge compensator.

When  $\text{Al} > \text{Na}$   
Al with higher coordination 5-6

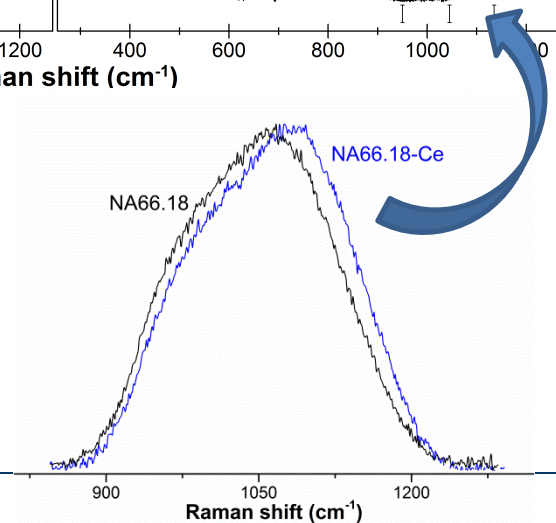
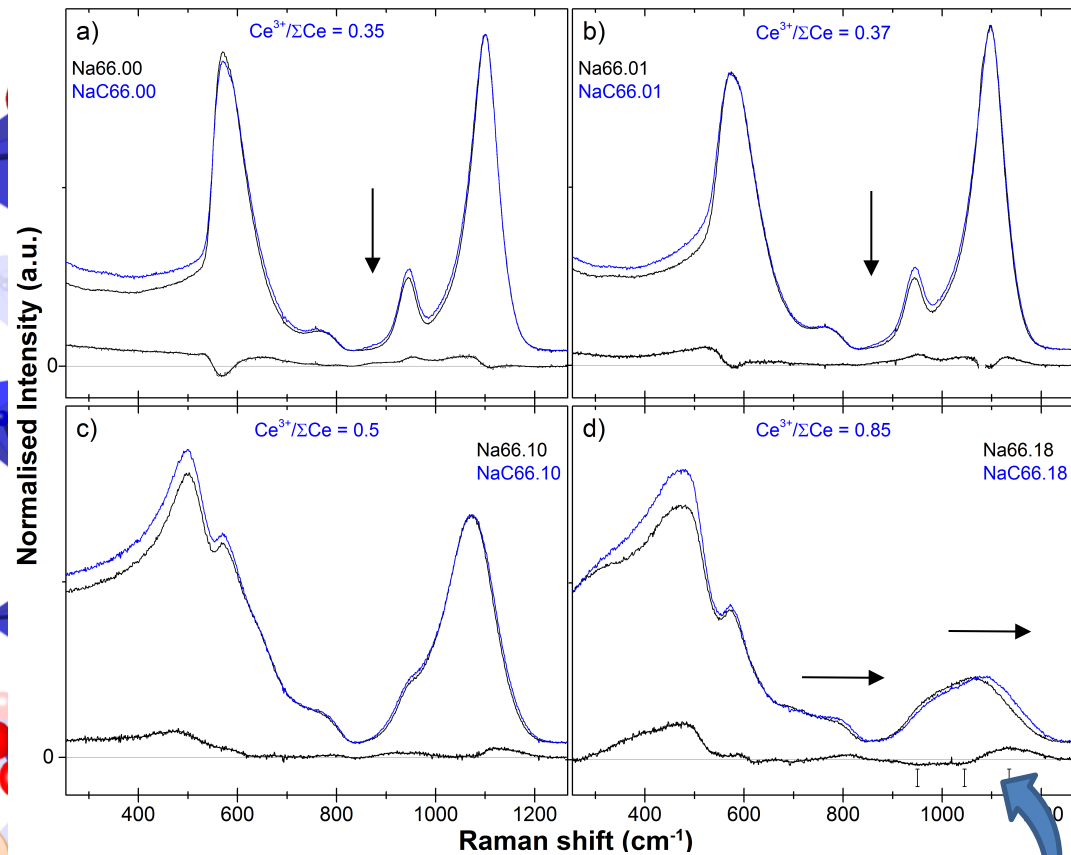
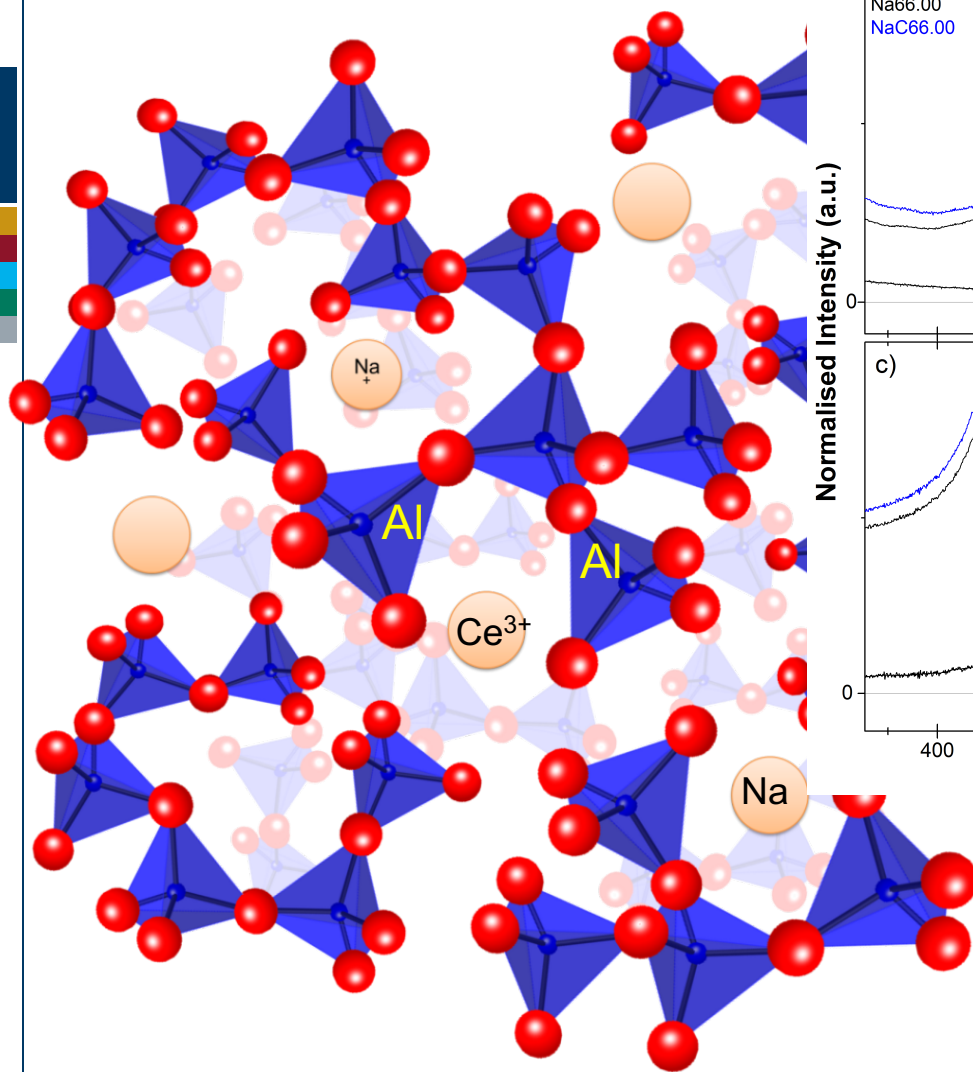


Deconvolutions of the Raman bands between 850 and 1300  $\text{cm}^{-1}$ , related to Si-O stretching in different  $Q^n$  tetrahedral units

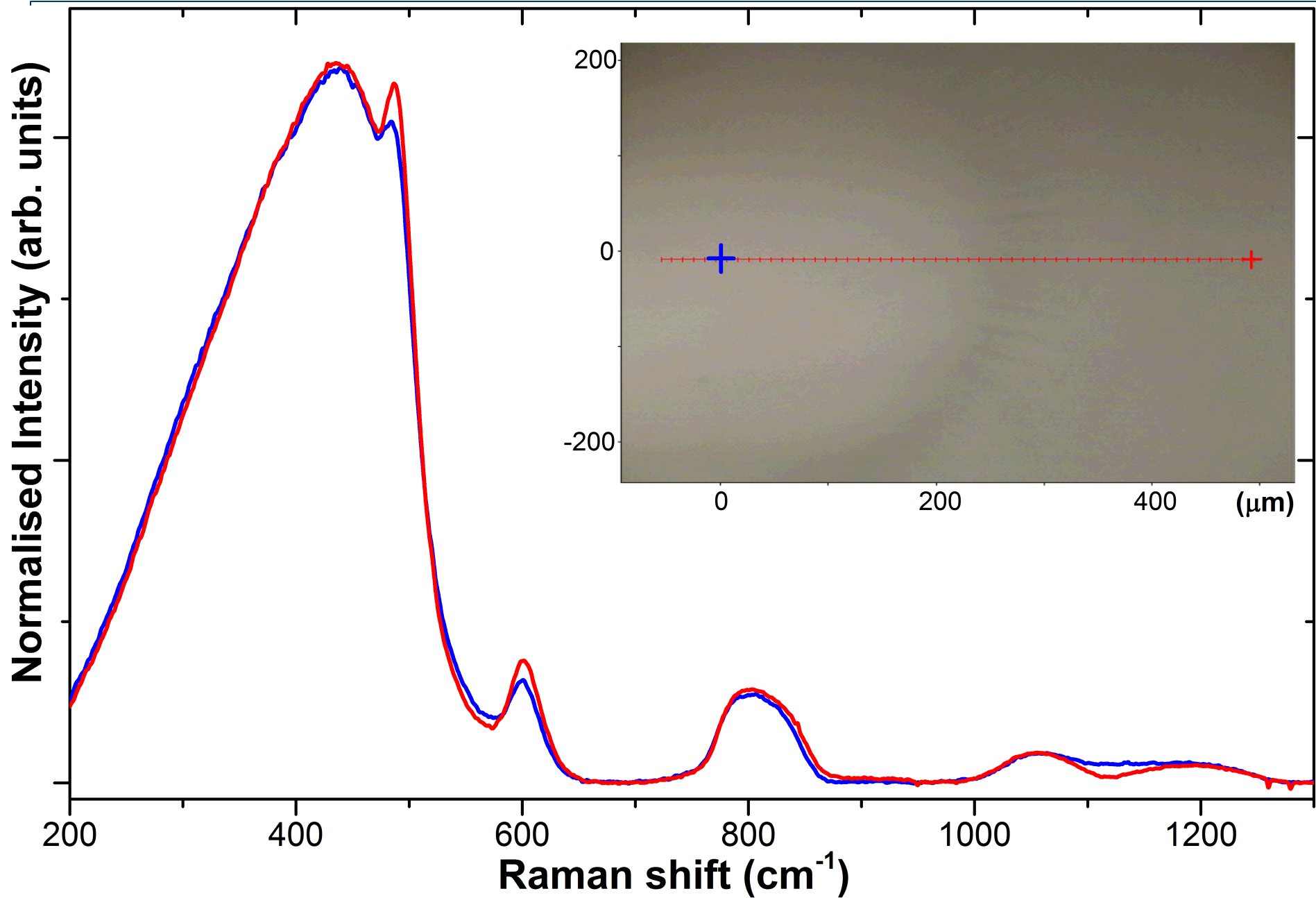


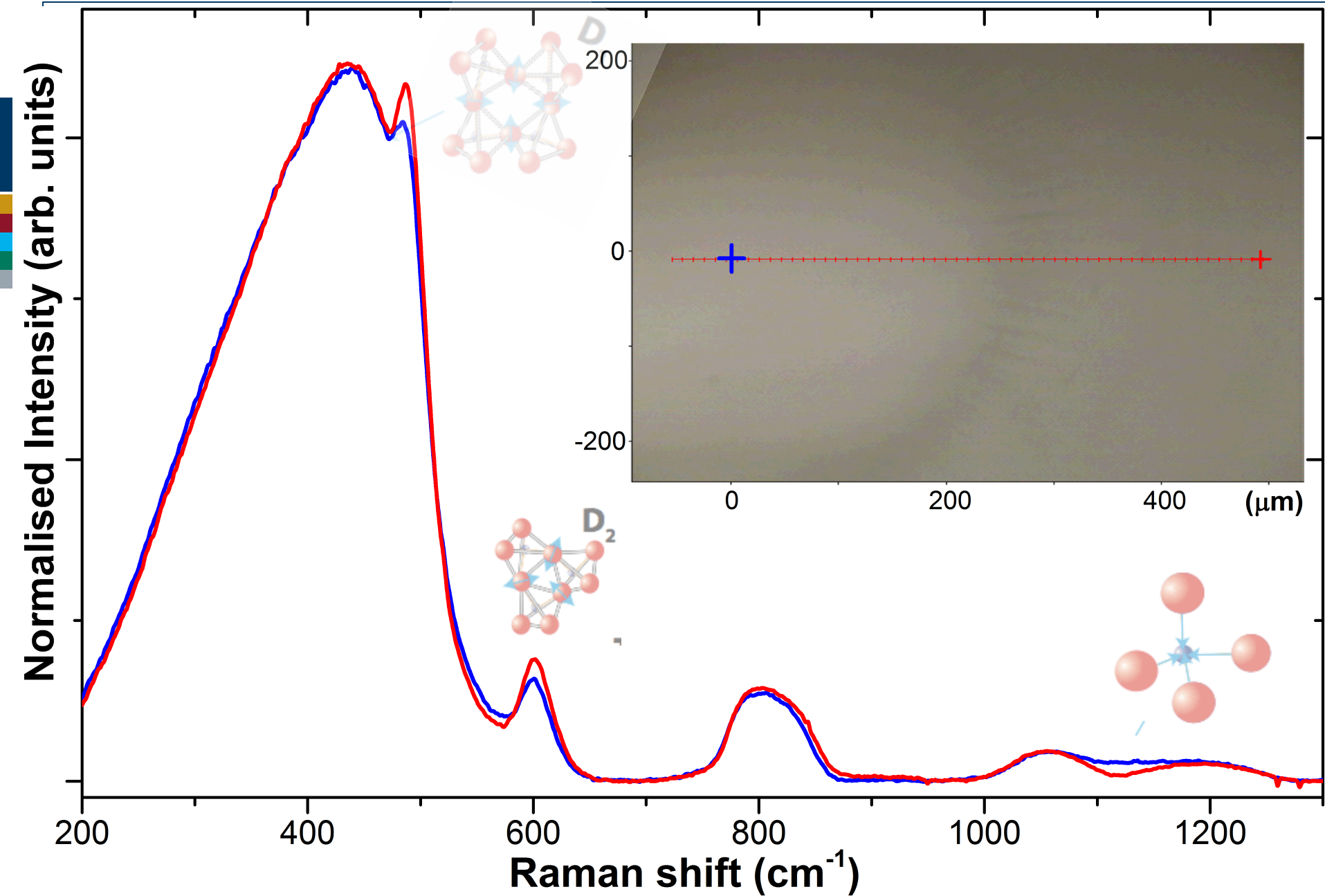


# Raman $\rightarrow$ NAC66.y glasses



$[6]\text{Ce}^{3+} = 1.01\text{\AA} = [6]\text{Na}^{+} \rightarrow \text{charge compensator}$







## \*X-ray Absorption Spectroscopy – XAS

XAS and D-XAS @ Ce L<sub>III</sub>-edge

- \* Redox kinetic (evolution with time) for different glass/melt polymerizations
- \* Redox ratio for Al-free and -bearing silicate glasses
- \* Redox ratio for Ce-activated fiber preforms

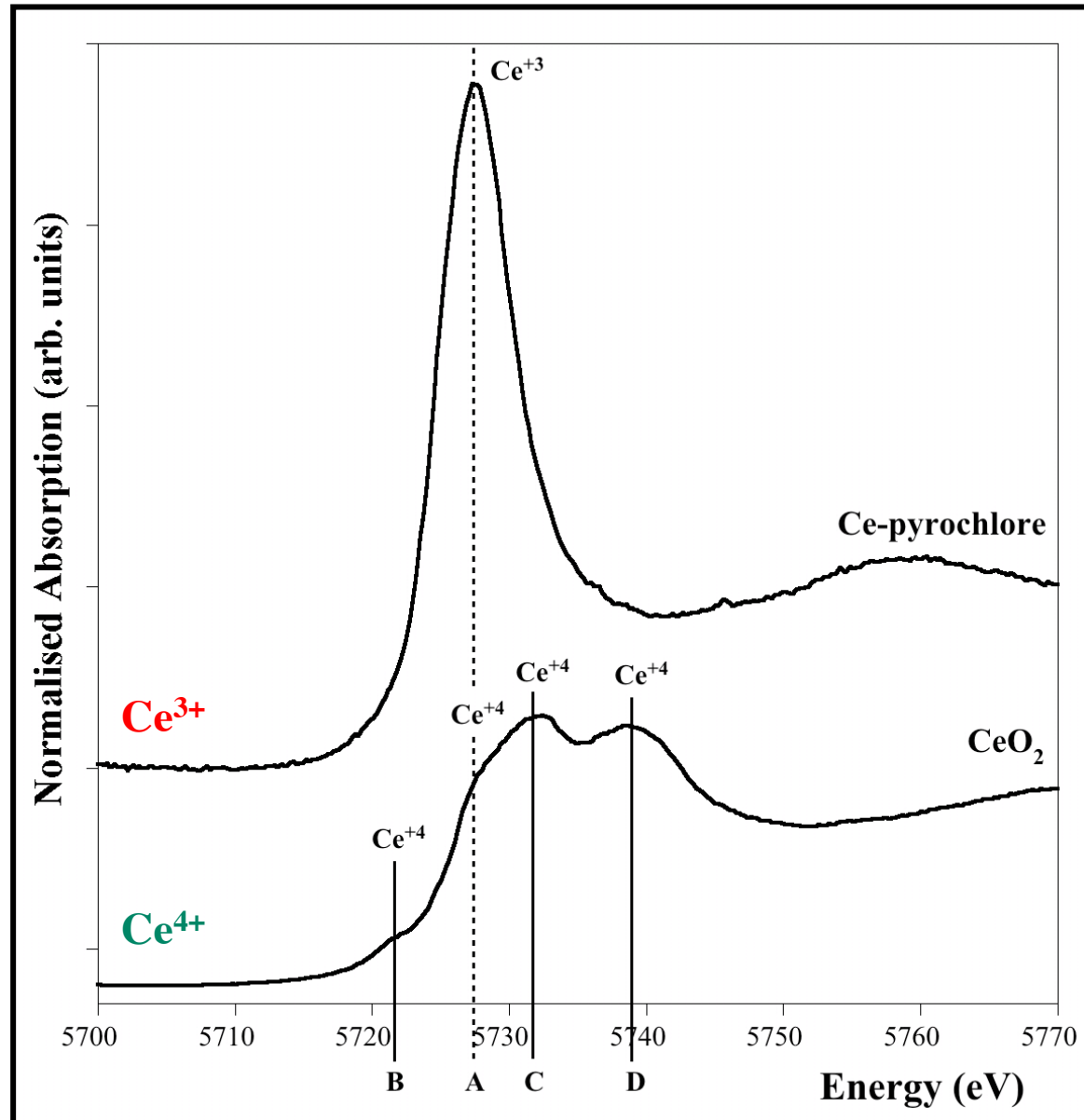
## \*Photoluminescence (PL)

- On the NA66-yy Serie
- Preform with different collapse condition and Al content

The different spectra for  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  can be used as fingerprint for the presence of both species

$\text{Ce}^{3+}$  model compounds have a narrow white-line at  $\sim 5727$  eV

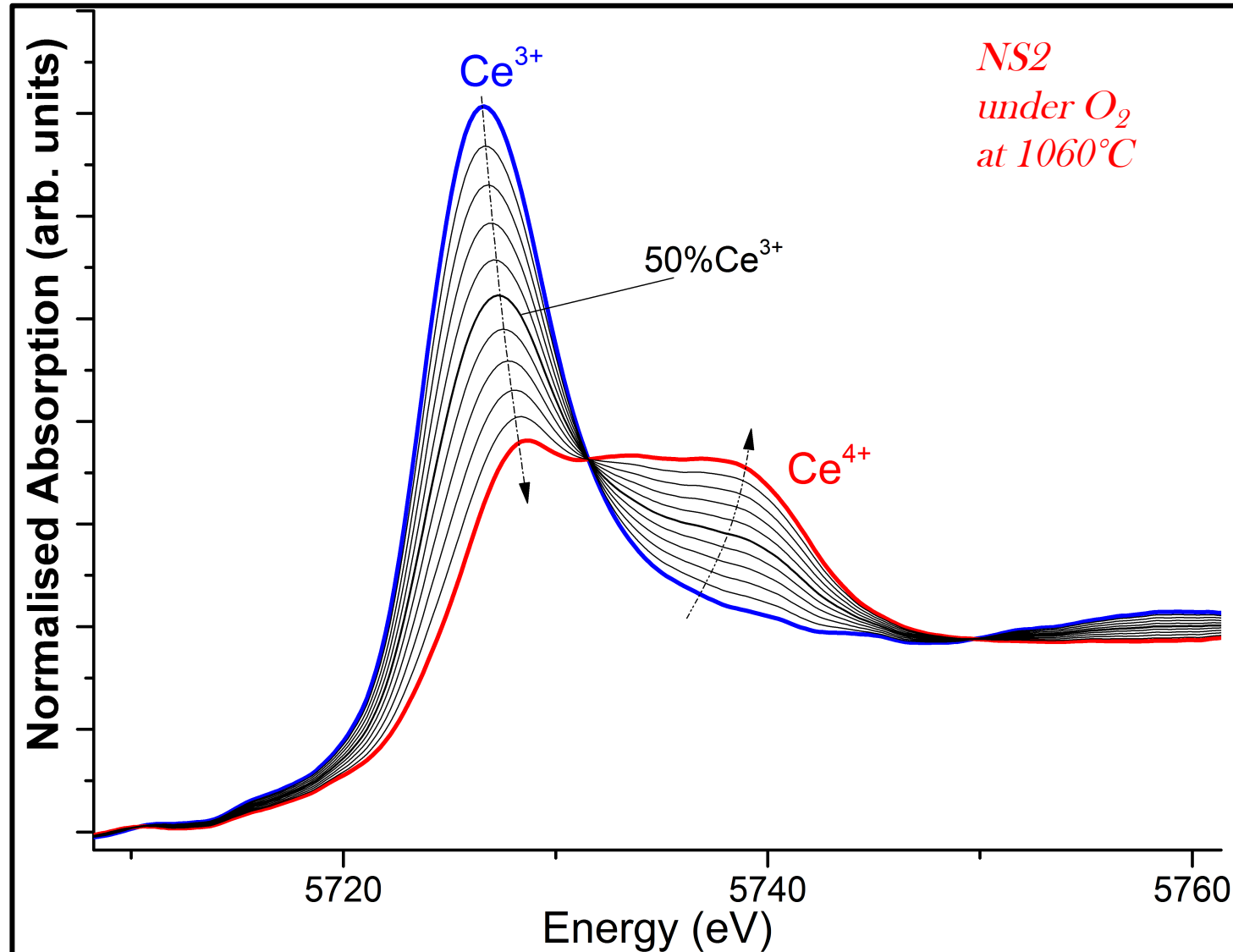
$\text{Ce}^{4+}$  model compounds have several features, corresponding to other electronic transitions

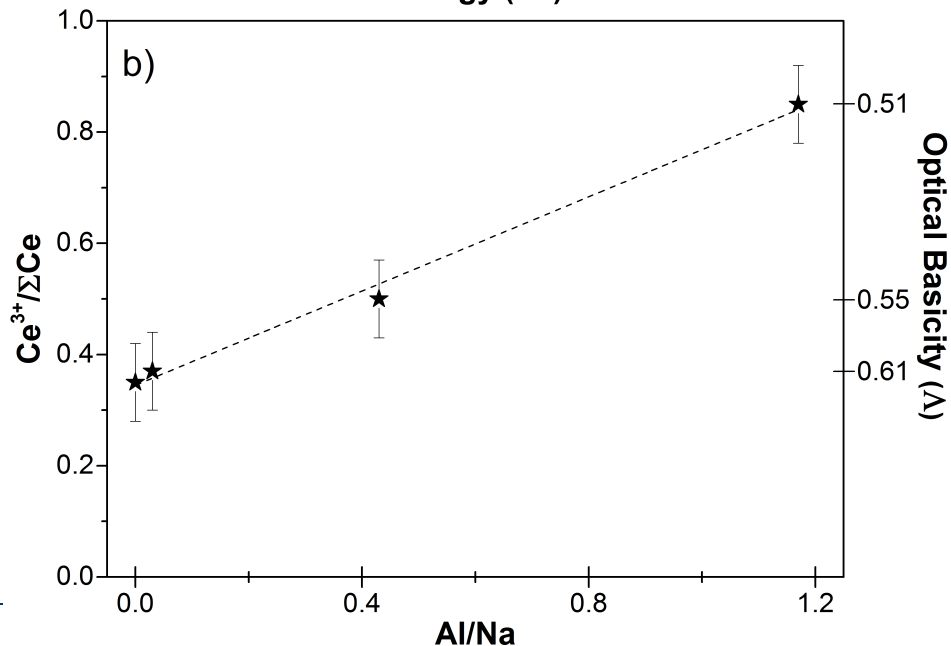
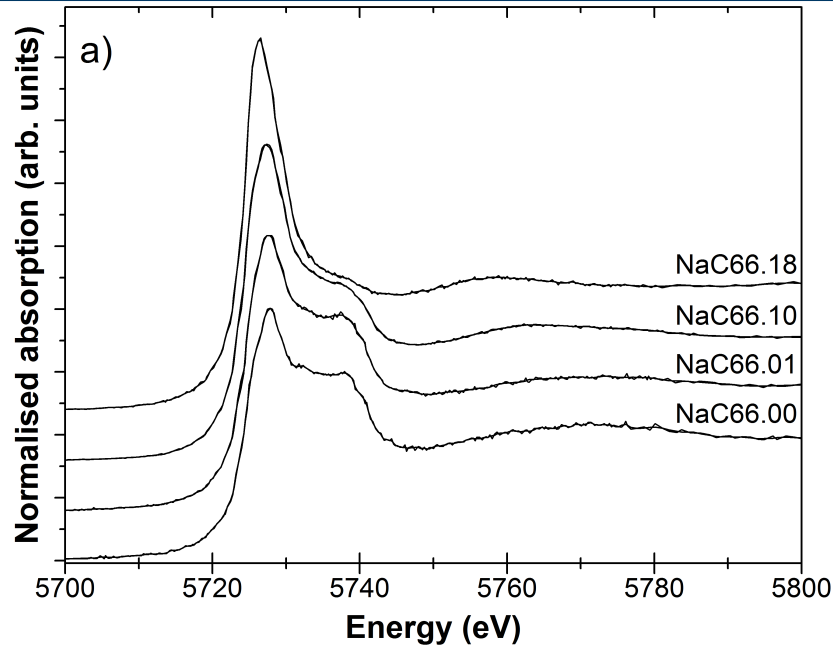




Evolution of  $\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$  ratio in NS2 melt

Linear combination  
of the  $\text{Ce}^{3+}$   
and  $\text{Ce}^{4+}$   
end-members



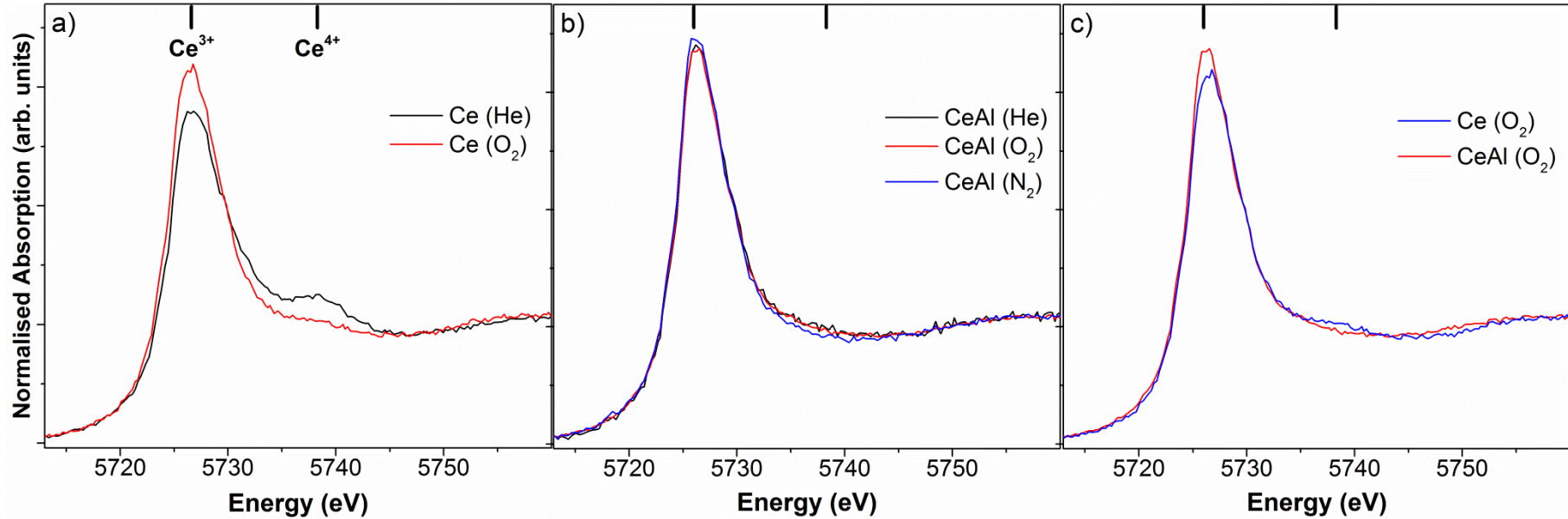


NAS glasses  
+ 0.36mol%  $\text{CeO}_2$

Synthesis at  $1400^\circ\text{C}$   
 $\text{P}_{\text{O}_2}$  in air

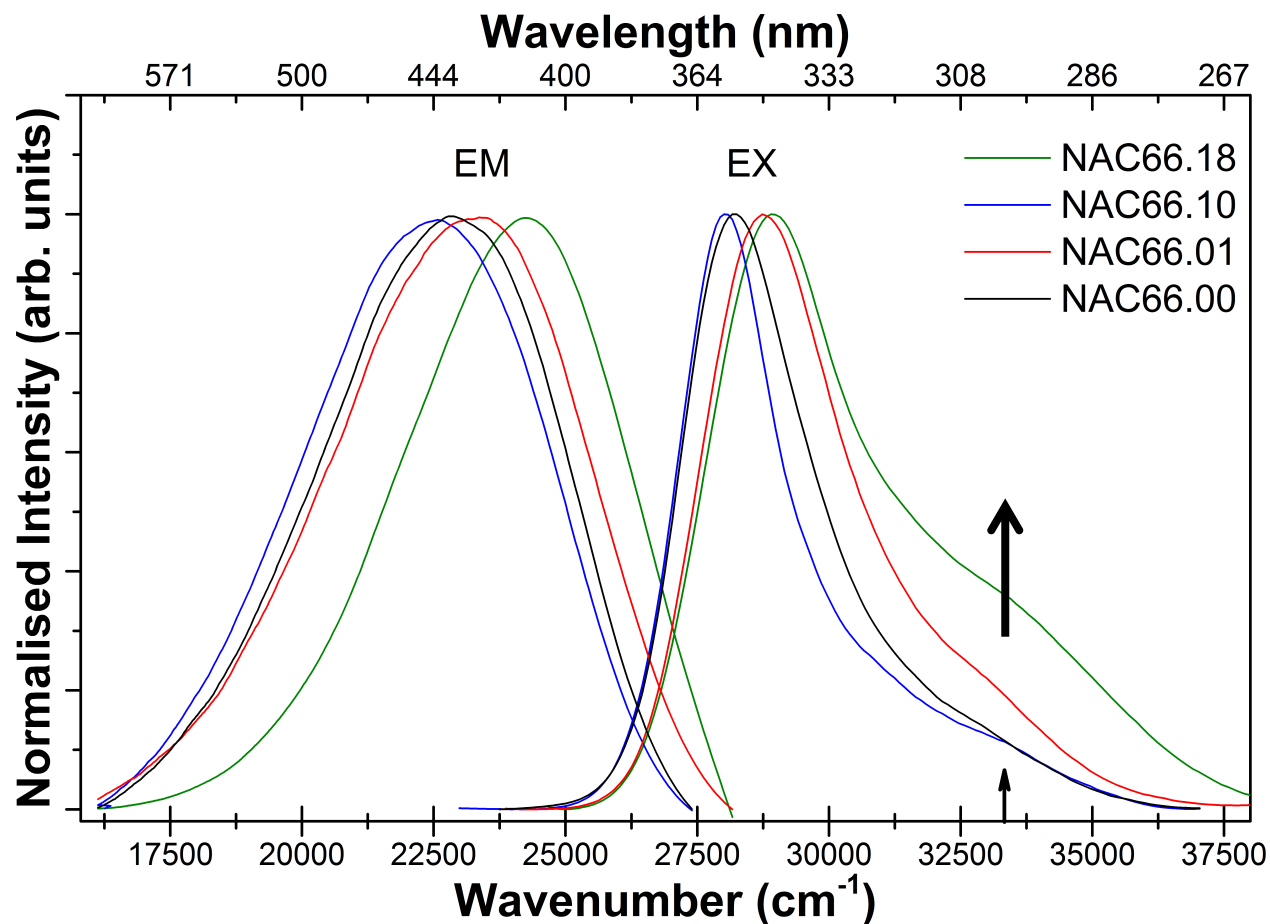
$\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$  in glasses  
vs.  
Al/Na molar ratio

Correlation between  $\text{Ce}^{3+}/\Sigma\text{Ce}$  redox ratio and both Al/Na molar ratio and theoretical optical basicity ( $\Lambda$ ).



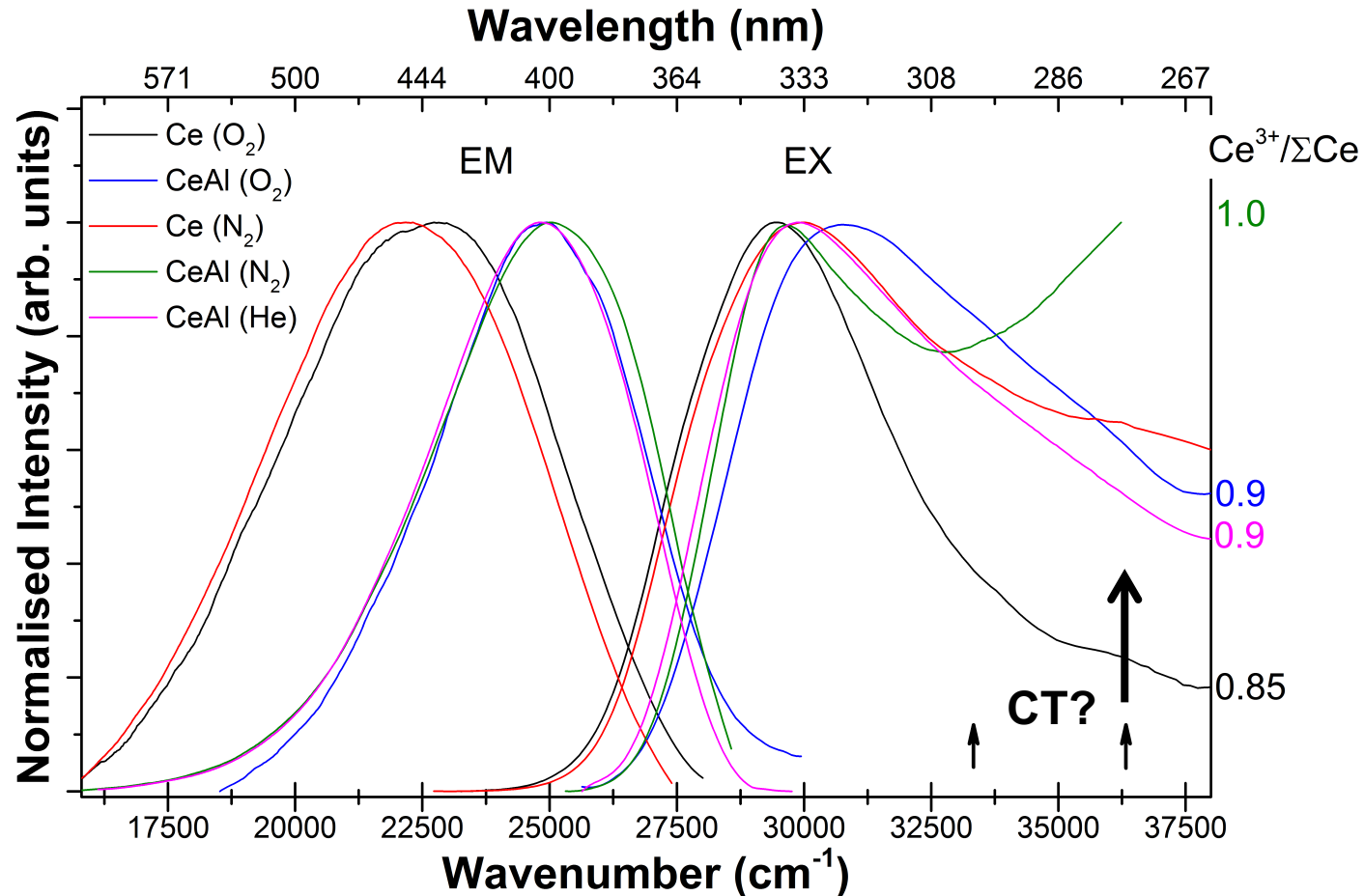
The driving force is the Al content/presence,  
and not the collapsing conditions

$\text{Ce}^{3+}$   
emission and  
excitation bands



\*Two groups (Al free and NA66.10) and (NA66.01 and NA66.18)

- For group 2, the band at 300 nm clearly increases suggesting Charge Transfert

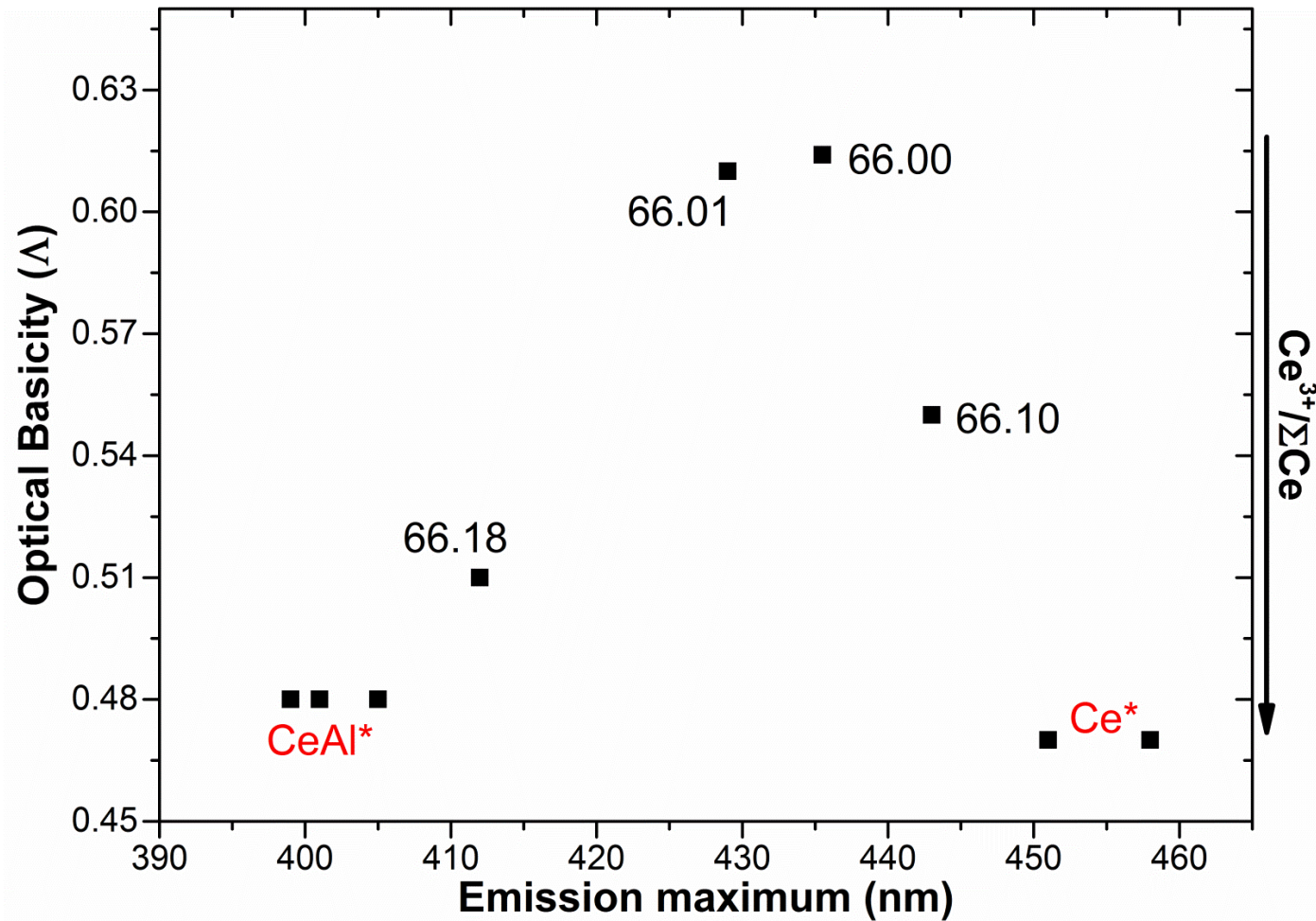


Different emission maxima depending on the presence of Al:

- @ 400nm for Al-codoped
- @ 450nm for Al-free

Al at high CN +  $\text{Ce}^{3+}$

Stronger „CT“ in the case CeAl ( $\text{N}_2$ )



\* Fiber preforms



19



\* Stabilization of reduced species with Al incorporation can be seen as a greater capacity of  $\text{Ce}^{3+}$  to behave as CC for Al compared to Na.

\* bands @275nm, in our samples, occurs only for low amount of  $\text{Ce}^{4+}$  ( $\text{Ce}^{3+}/\text{Ce}_{\text{tot}} > 0.85 \pm 0.07$ ).



\* Photo-darkening attenuation could be associated with :  
+ stabilization of higher amounts of  $\text{Ce}^{3+}$  in the amorphous structure,  
+ ability of trivalent Ce to trap hole centers,  
= reducing the formations of Al/Si defects

Need to check directly on photo-darkening experiment.

Optical basicity, Ce redox and optical properties can be correlated if we consider the different Al local surrounding



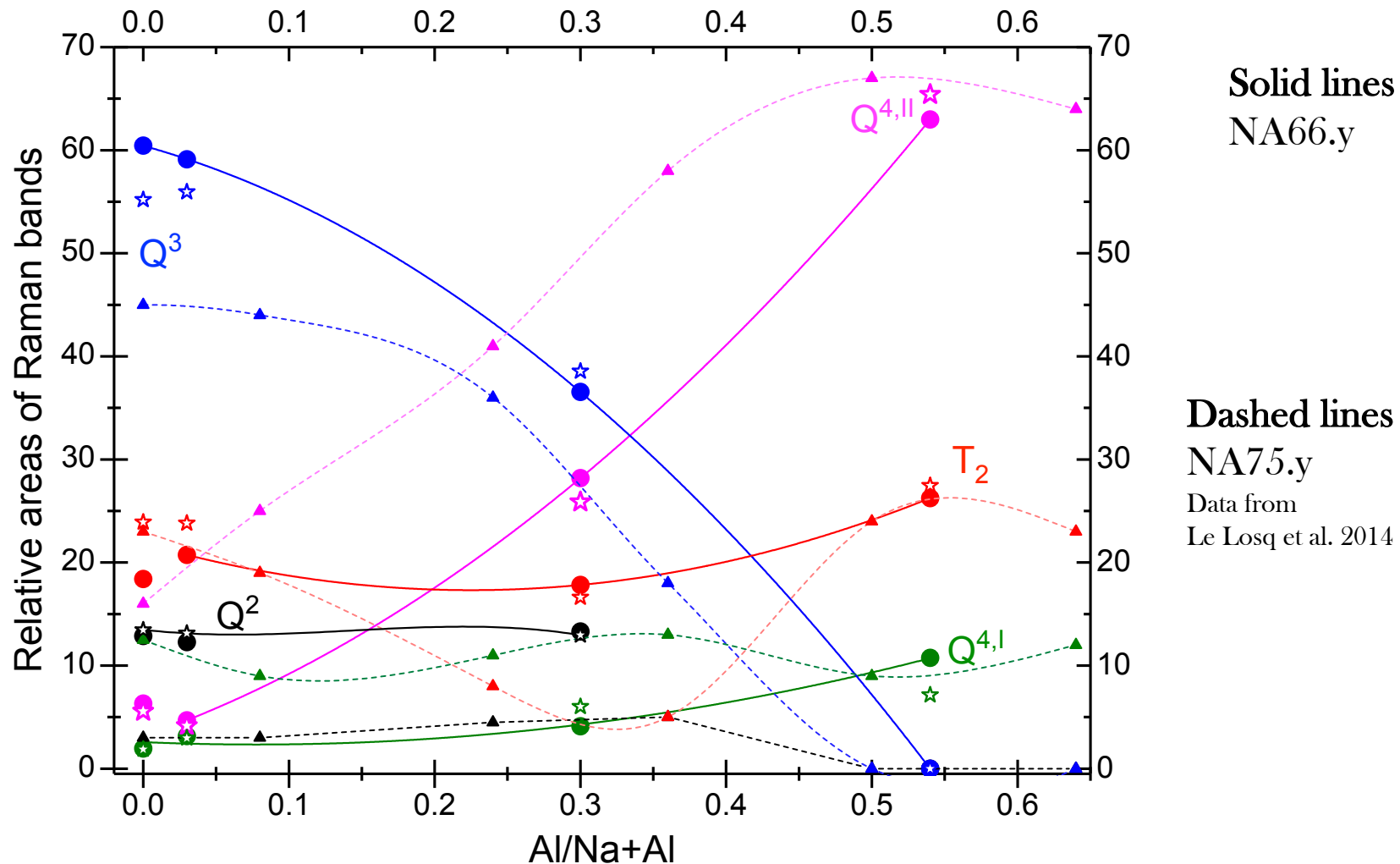
Cicconí et al. 2017

*In press*

10.1016/j.jnoncrysol.2017.08.035



## Evolution of the bands for NA66.y and Na75.y glasses



In going from peralkaline to peraluminous the bands have similar trends.

## Ce redox kinetic in melts

$\text{Ce}^{3+}/(\text{Ce}^{3+}+\text{Ce}^{4+})$  in melts vs. time

