

La structure des silicates fondus vu par la spectrométrie Raman

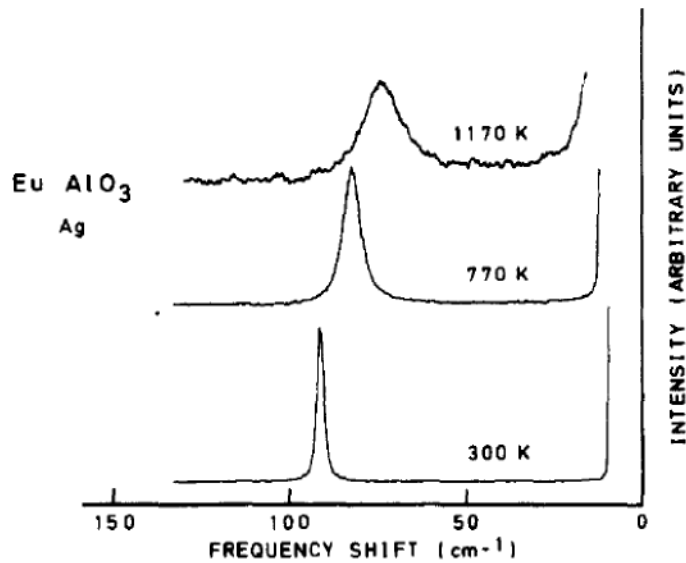
Daniel R. Neuville

neuville@ipgp.fr

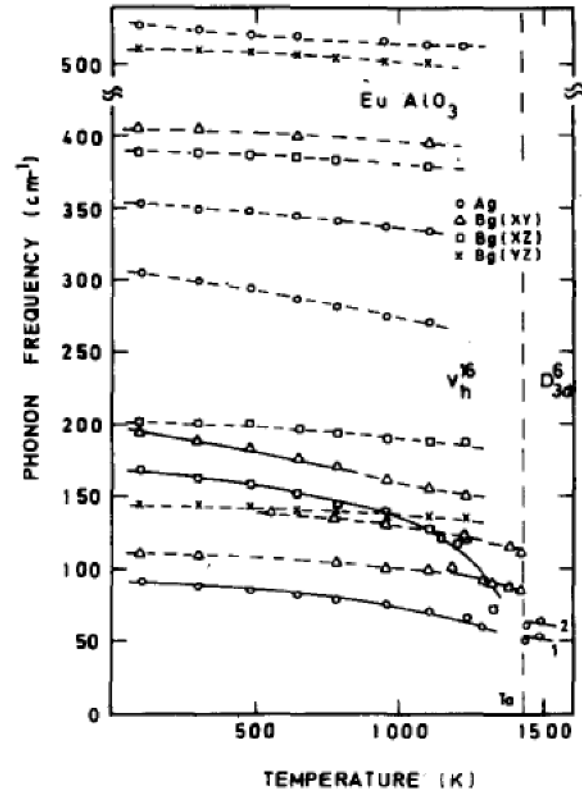


P. Alain et B. Piriou 1975 ...

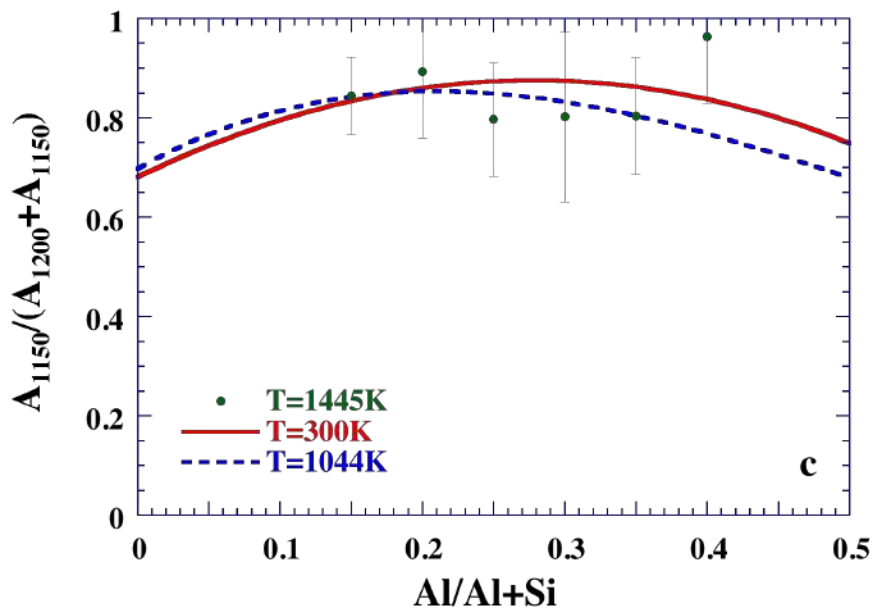
jusqu'à 1500°C sur des composés cristallins pour suivre des changements de phase dans EuAlO_3



Raman spectra of A_g soft mode at three different temperatures.



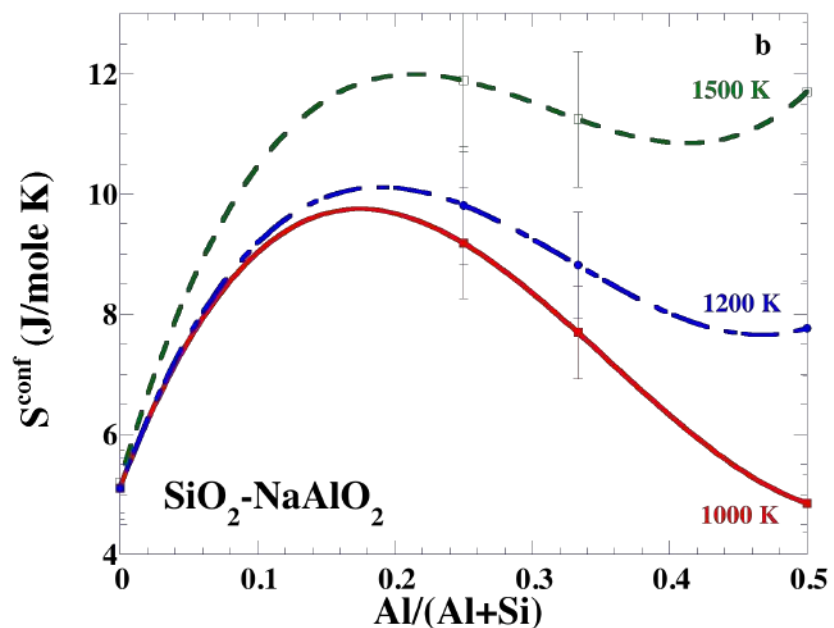
Experimental results for the temperature dependence of the Raman frequencies in EuAlO_3 . The notation refers to the axes of Raman tensors as described in the text. Curves are guides to eyes.



Raman à haute température...

Très difficile... mais ...

=> Lien fort entre structure et propriétés, η , S^{conf}



1^{er} Raman spectra

Fig. 6.—
Diffused by
Ground Glass.

The Production of New Radiations by Light Scattering.—Part I.

By Prof. C. V. RAMAN, F.R.S., and K. S. KRISHNAN.

VOLUME 38

(Received August 7, 1928.)

THE MOLECULAR SCATTERING OF LIGHT FROM AMORPHOUS AND CRYSTALLINE SOLIDS

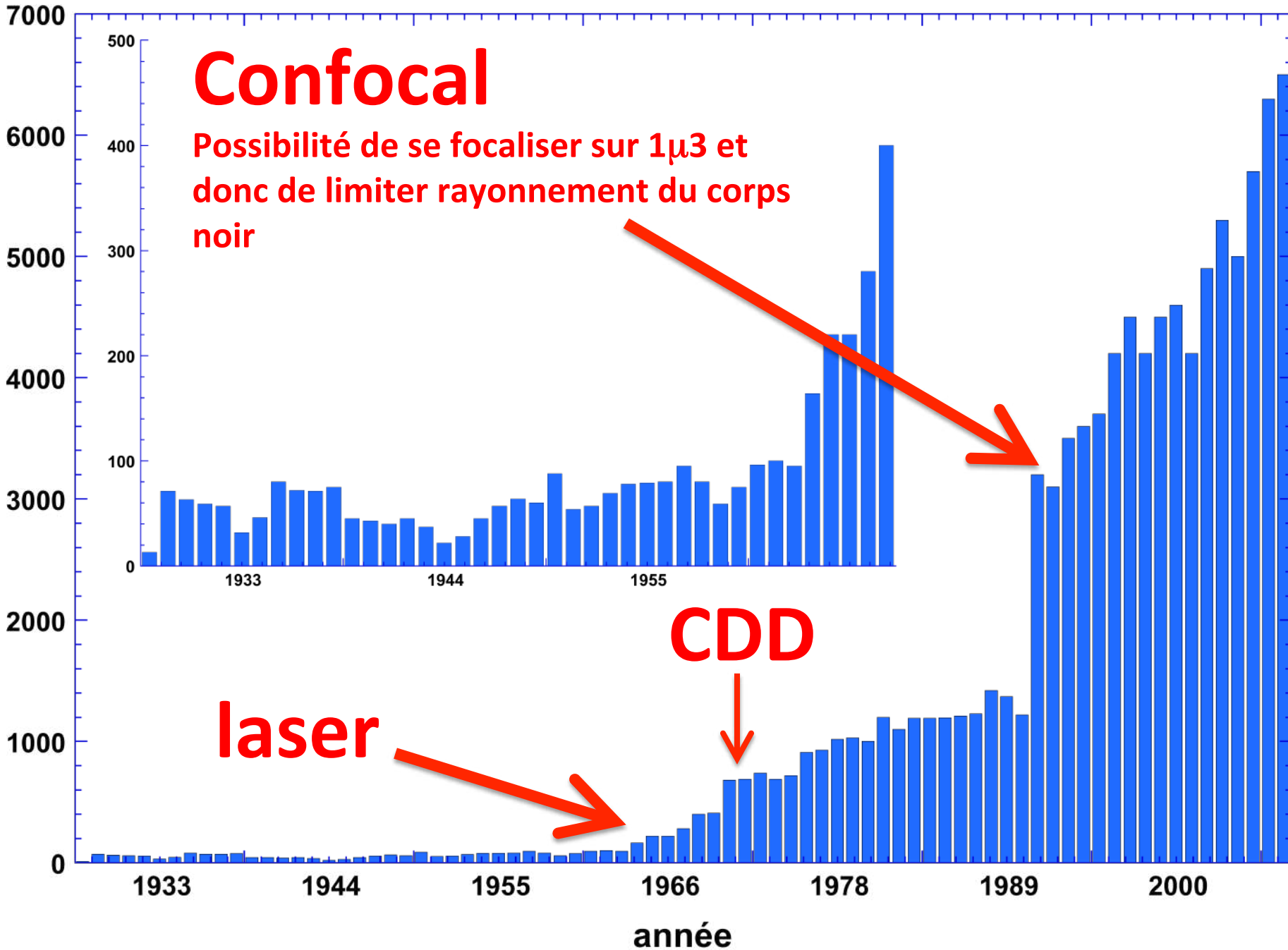
BY ALEXANDER HOLLAENDER AND JOHN WARREN WILLIAMS
LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN

(Received September 22, 1931)

Exciting line	Excited line	$\Delta\nu$	λ
4358	4718	1748	5.7
	4682	1585	6.3
	4619	1293	7.7
	4572*	1071	9.3
	4513	785	12.7
	4485	647	15.5
	4463	537	18.6
	4450	471	21.2
	4408	259	38.6

* This is the most intense band. The microphotograph indicates that it may possibly be resolved into three lines, with the most intense one in the center.

nombre d'article portant sur la spectroscopie Raman



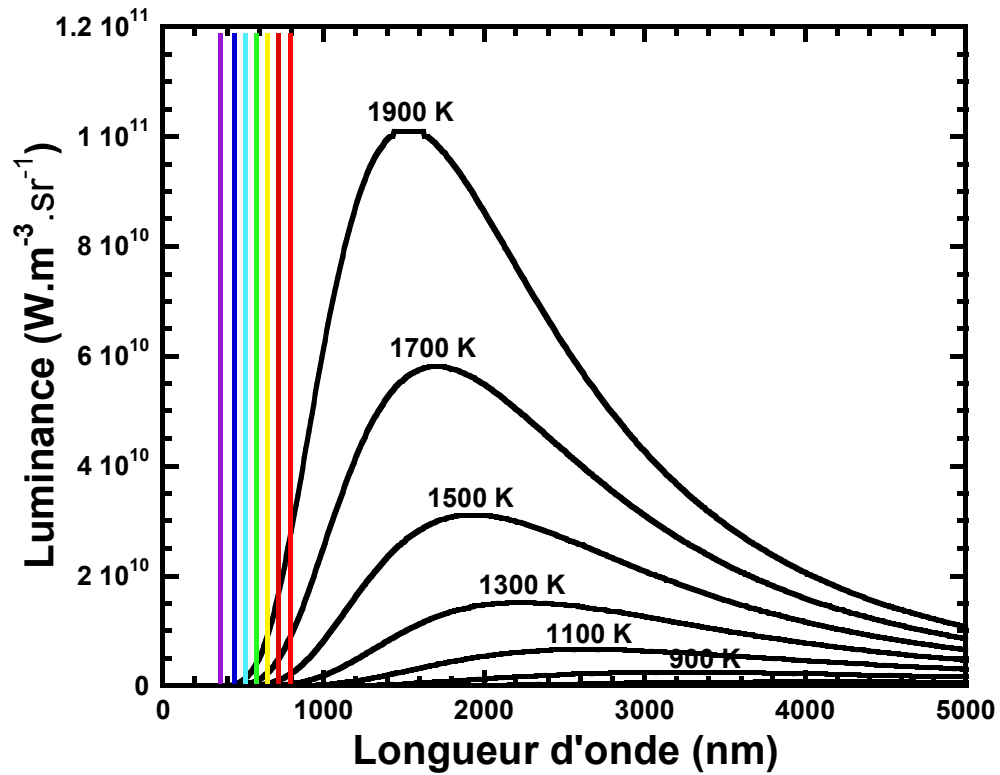
Confocal

Possibilité de se focaliser sur $1\mu^3$ et donc de limiter rayonnement du corps noir

CDD

laser

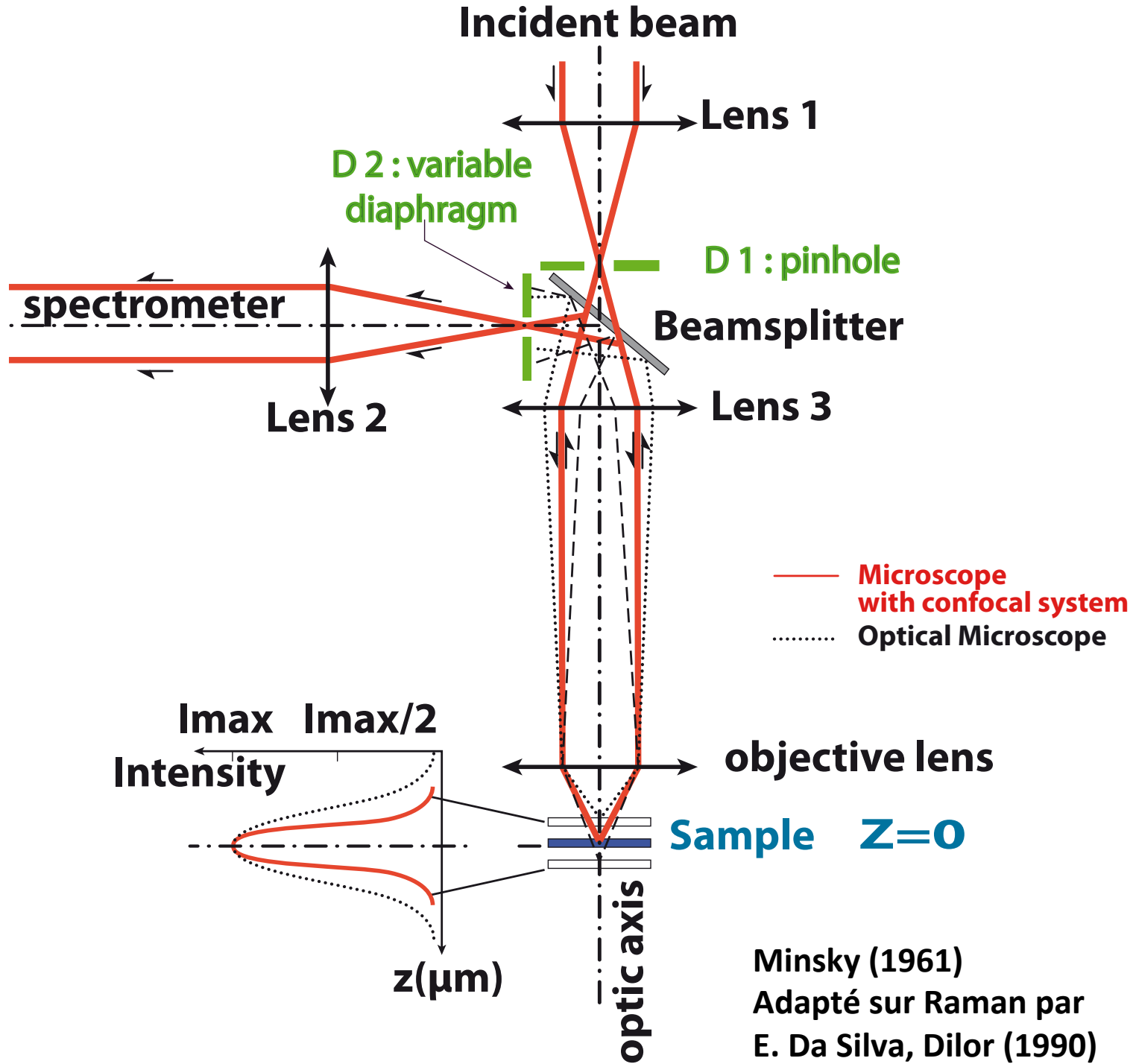
année

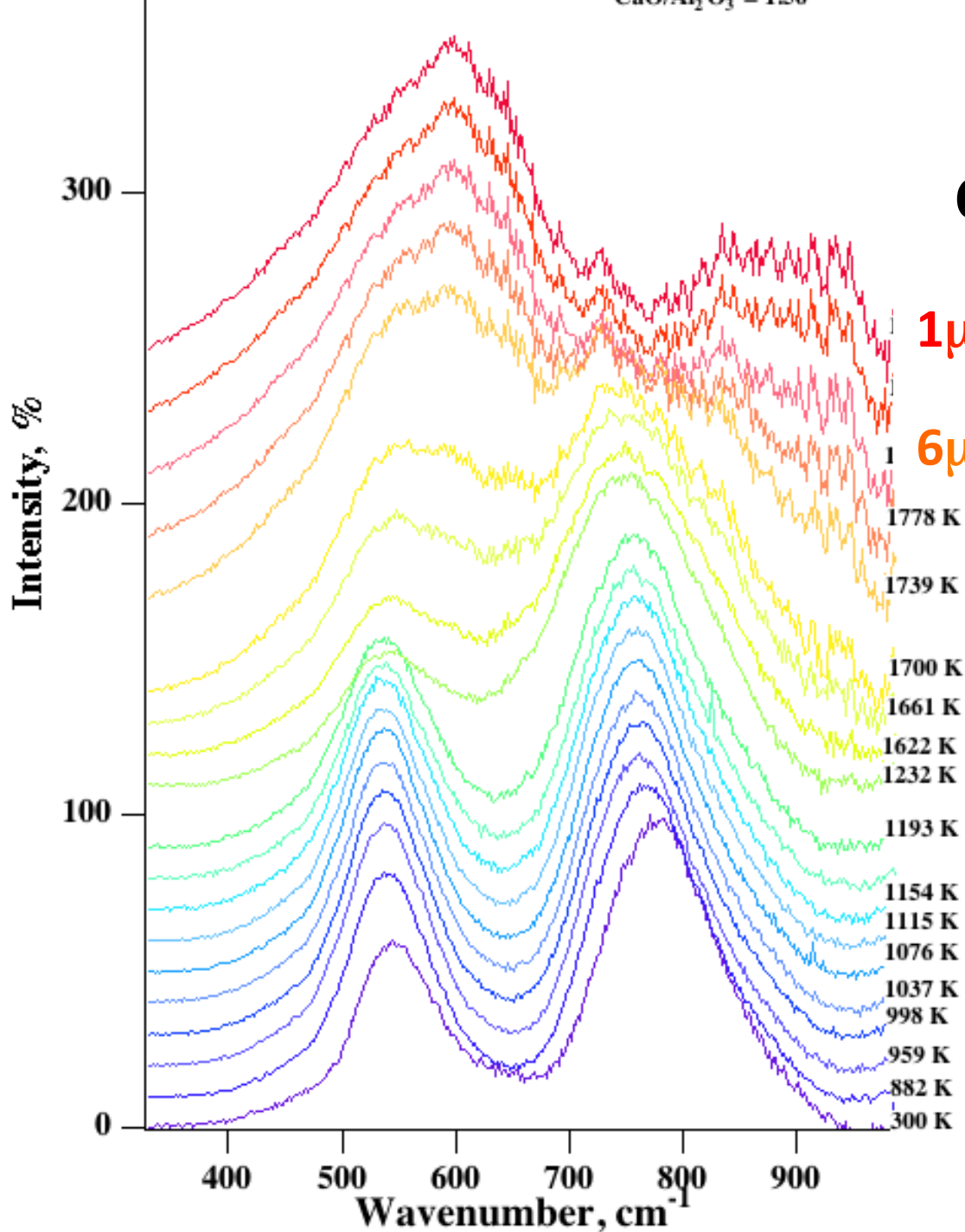


Loi de Wien

$$L = \frac{2hc^2}{\lambda^5} \cdot \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1}$$

$$\lambda_{max} = \frac{2,898 \cdot 10^{-3}}{T}$$





Confocal

C12A7

$1\mu\text{m}^3$

$6\mu\text{m}^3$

$T=1930\text{ K}$

Profondeur de pénétration

$$Pdp = 4\lambda/NA^2$$

λ : excitatrice

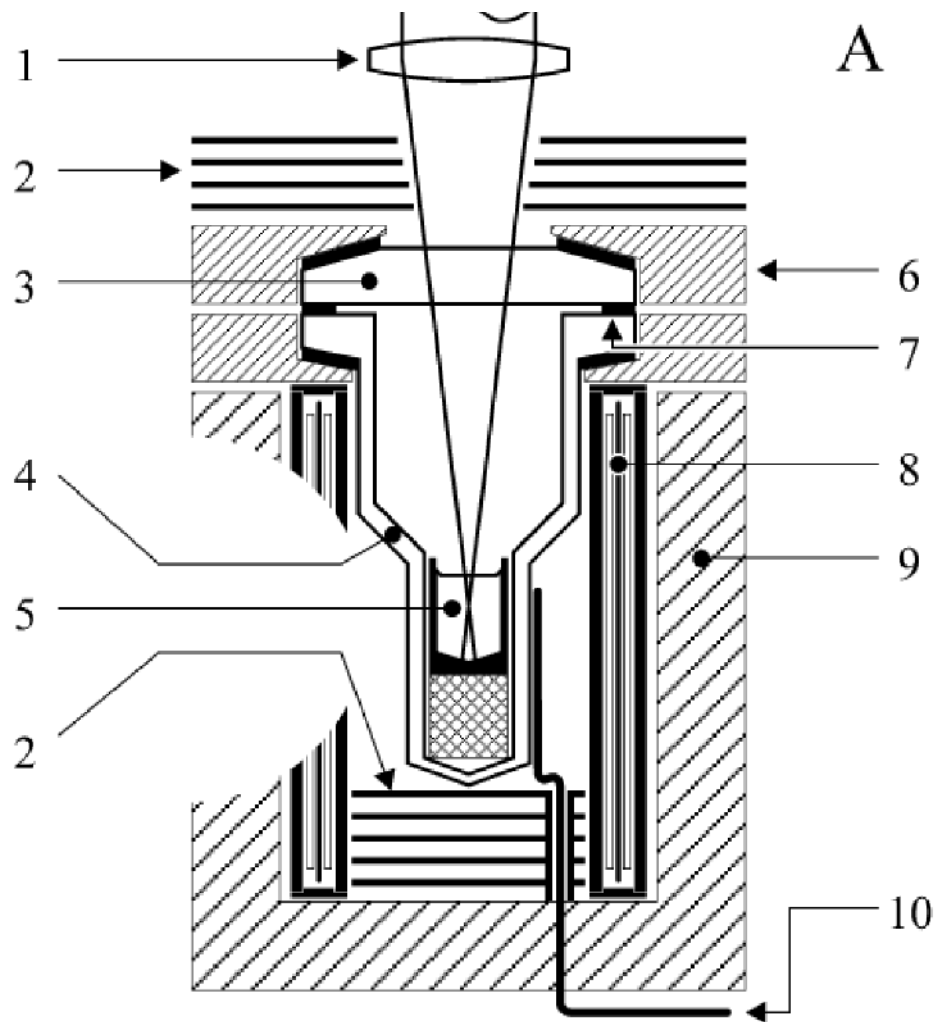
NA: ouverture numérique
définit par l'objectif
et confocal

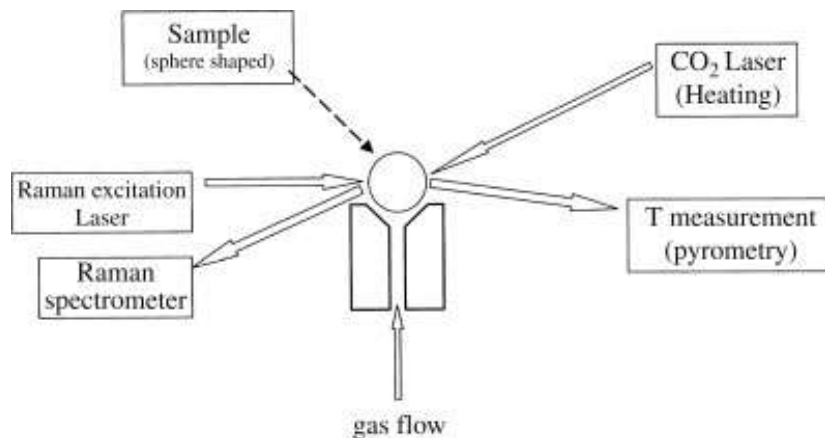
Diamètre du spot

$$D = 1.22\lambda / NA$$

Raman spectroscopic study of mixed valence neodymium and cerium chloride solutions in eutectic LiCl-KCl melts

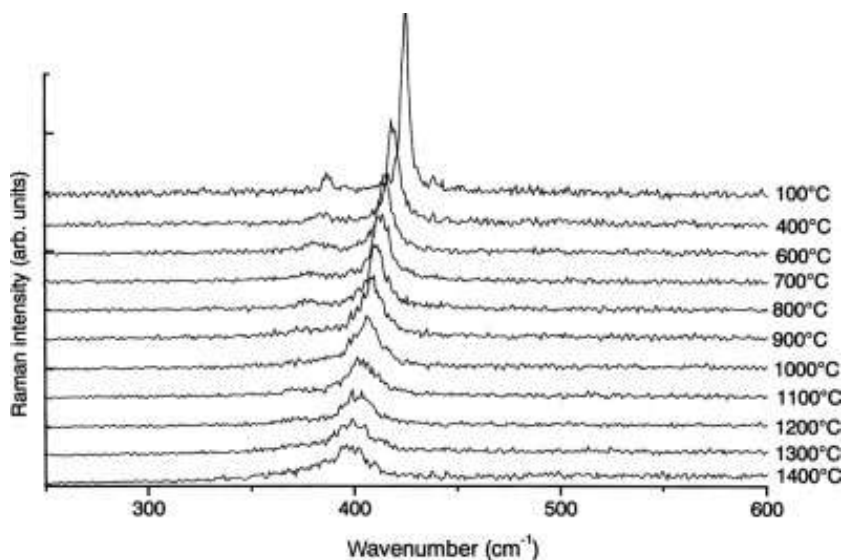
Veronica M. Rodriguez-Betancourt and Detlef Nattland*





JOURNAL OF RAMAN SPECTROSCOPY
J. Raman Spectrosc. 2003; **34**: 497–504
 Published online in Wiley InterScience
 (www.interscience.wiley.com). DOI:
 10.1002/jrs.1020

High temperatures and Raman scattering through pulsed spectroscopy and CCD detection
P. Simon et al.



Raman spectra of Al₂O₃ ceramics, in micro configuration (heating in furnace), recorded with the ICCD device. Acquisition time, 10 s.

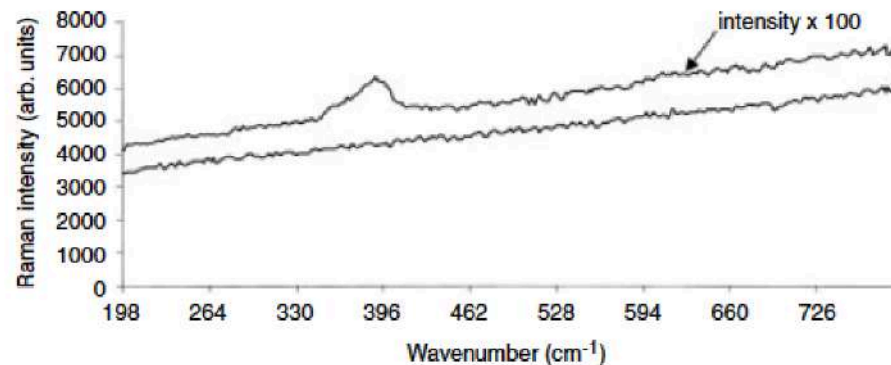
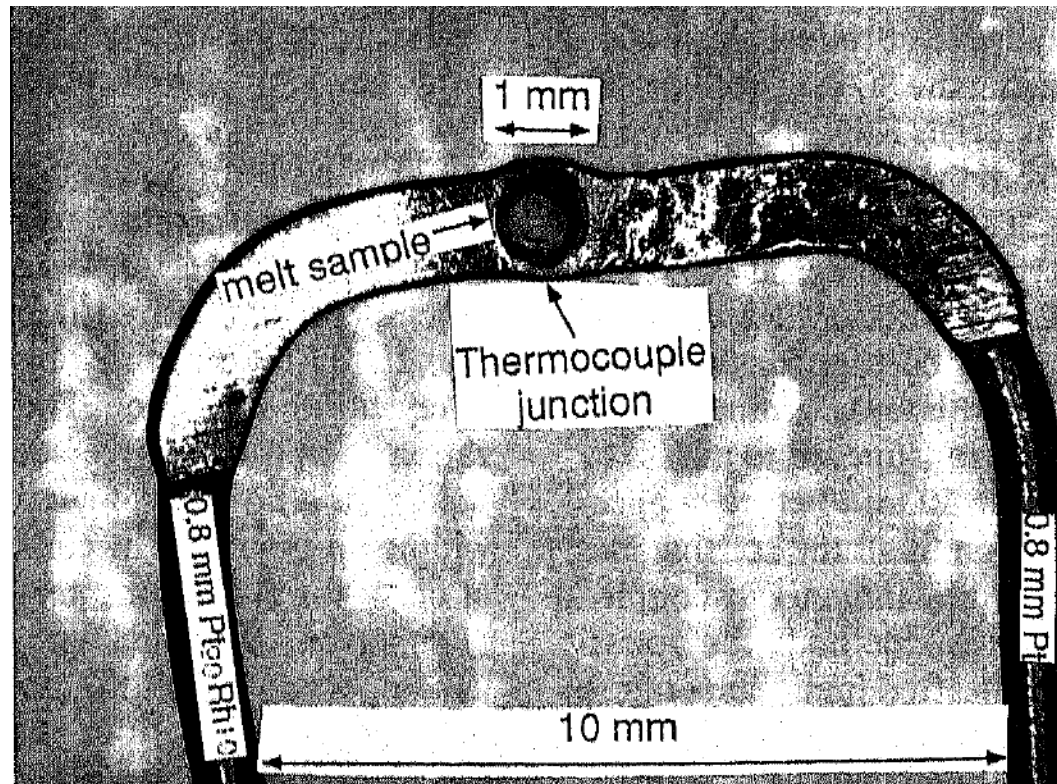


Figure 6. Raman spectra of Al₂O₃ ceramics, in macro configuration, with a CO₂ laser, recorded with the Pockels switch device. The lower curve was recorded with parallel polarizers and no voltage on the Pockels cell (acquisition time 0.1 s). The upper curve was recorded with perpendicular polarizers and the Pockels cell synchronized on the laser pulse (acquisition time 10 s, 100 times longer than the previous one).

Raman spectroscopy of silicate melts at magmatic temperatures: $\text{Na}_2\text{O}-\text{SiO}_2$, $\text{K}_2\text{O}-\text{SiO}_2$ and $\text{Li}_2\text{O}-\text{SiO}_2$ binary compositions in the temperature range 25–1475°C

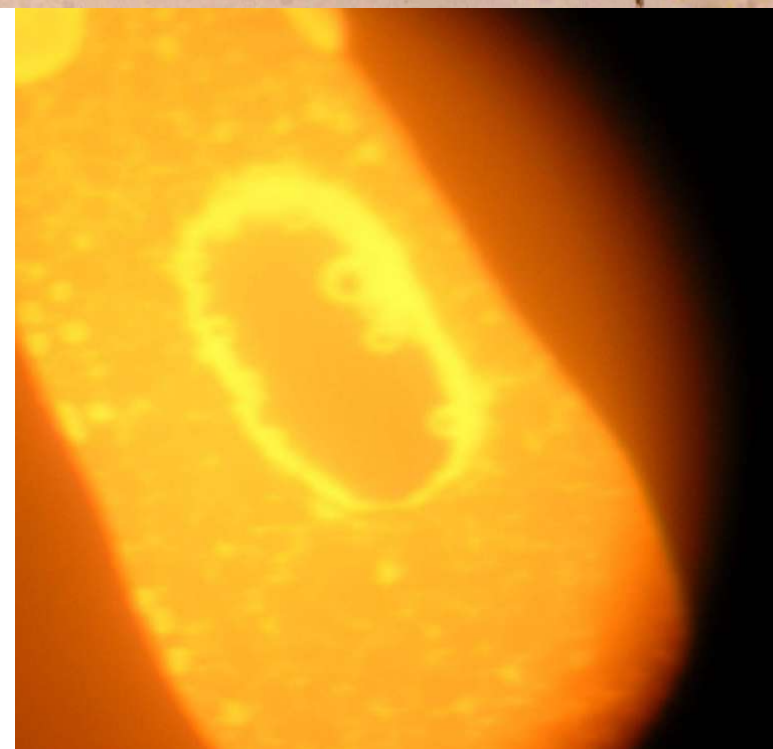
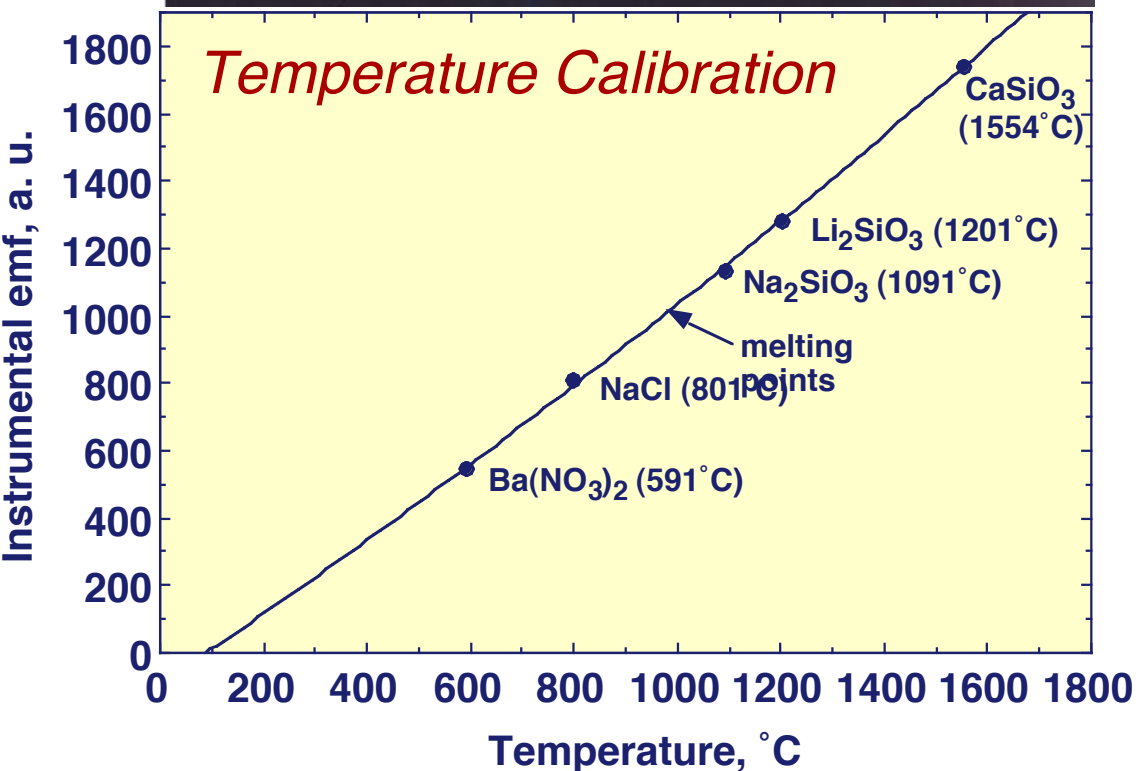
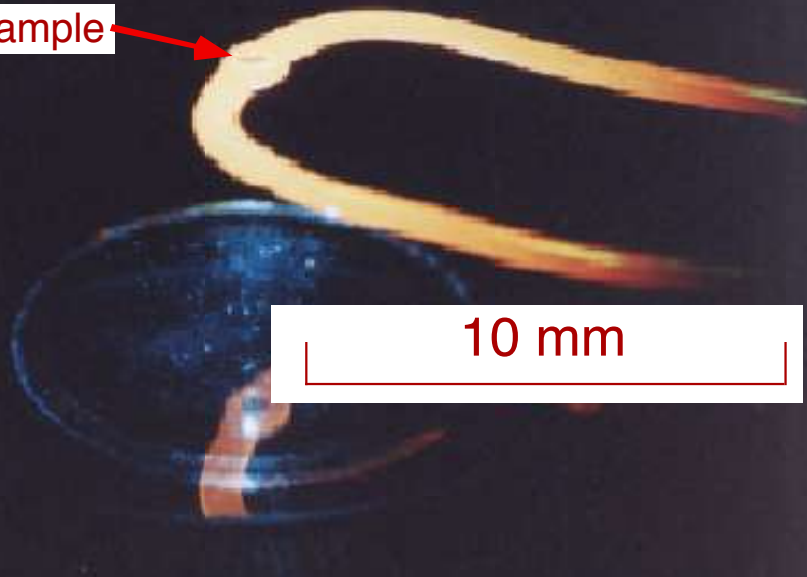
Bjorn O. Mysen and John D. Frantz

Geophysical Laboratory, 5251 Broad Branch Rd., N.W., Washington, DC 20015, USA



High-T Microfurnace

Sample

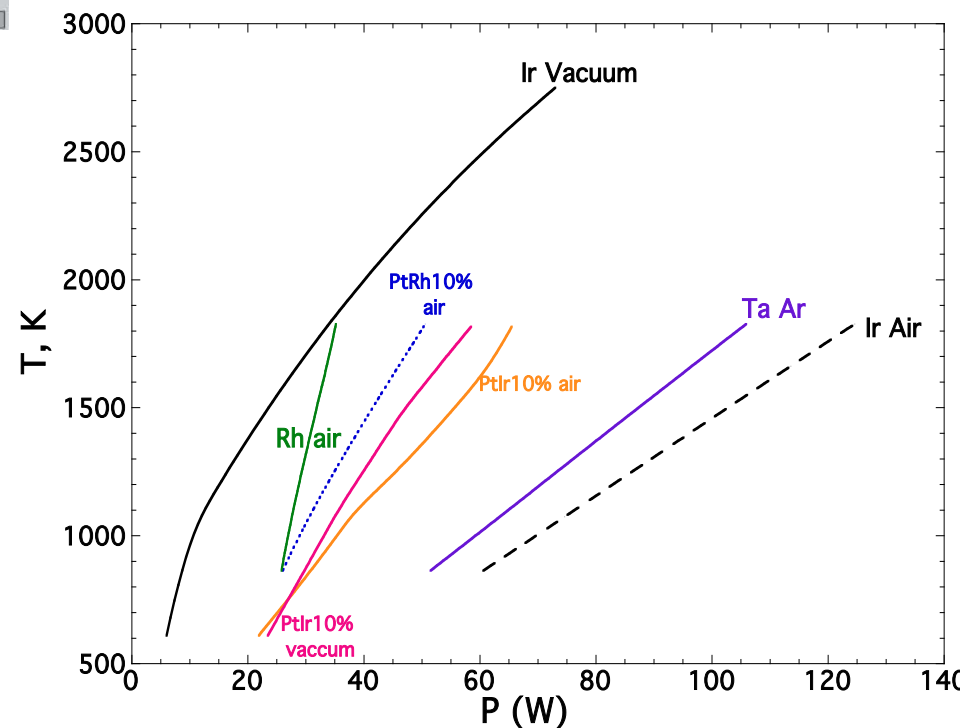
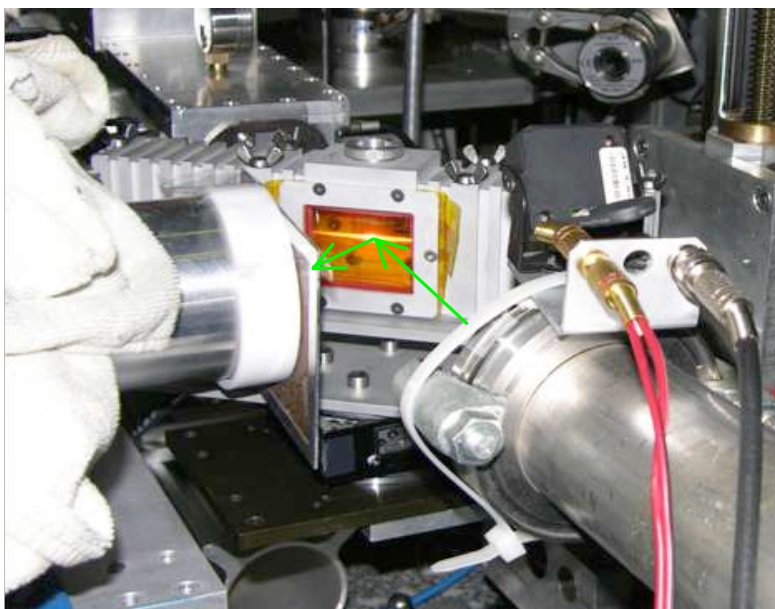
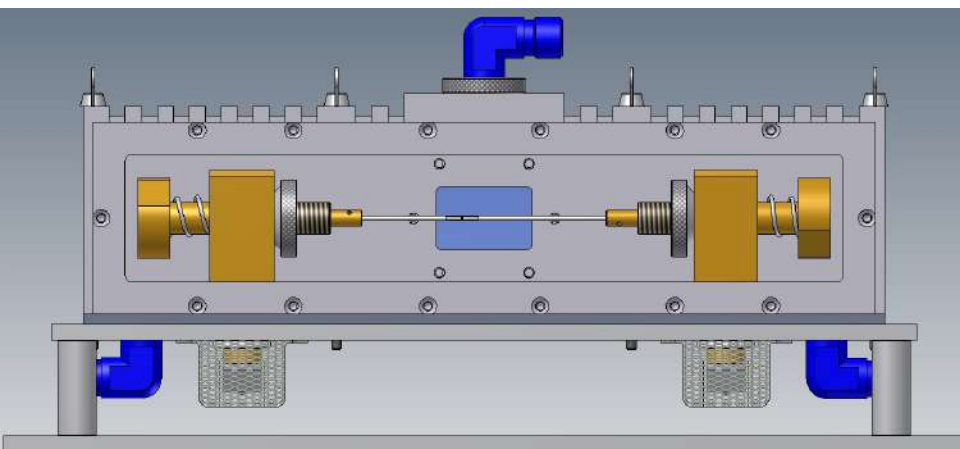




Bulle



1^{er} cristal



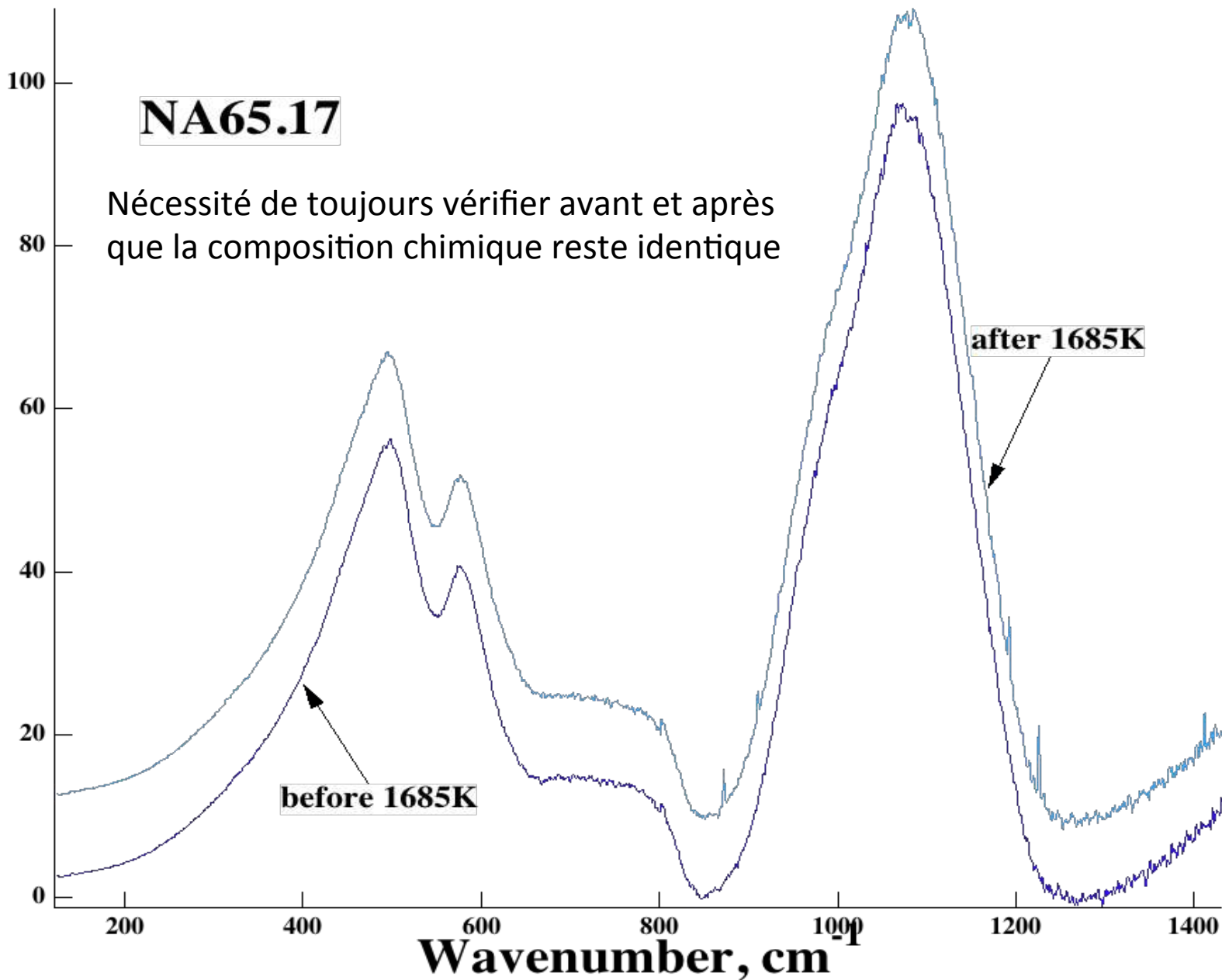
- ✓ Fil en métal unique : Pt, PtRh10%, PtIr10%, PtIr20%, Ta, Rh, W
- ✓ Fil droit
- ✓ différent atmosphère

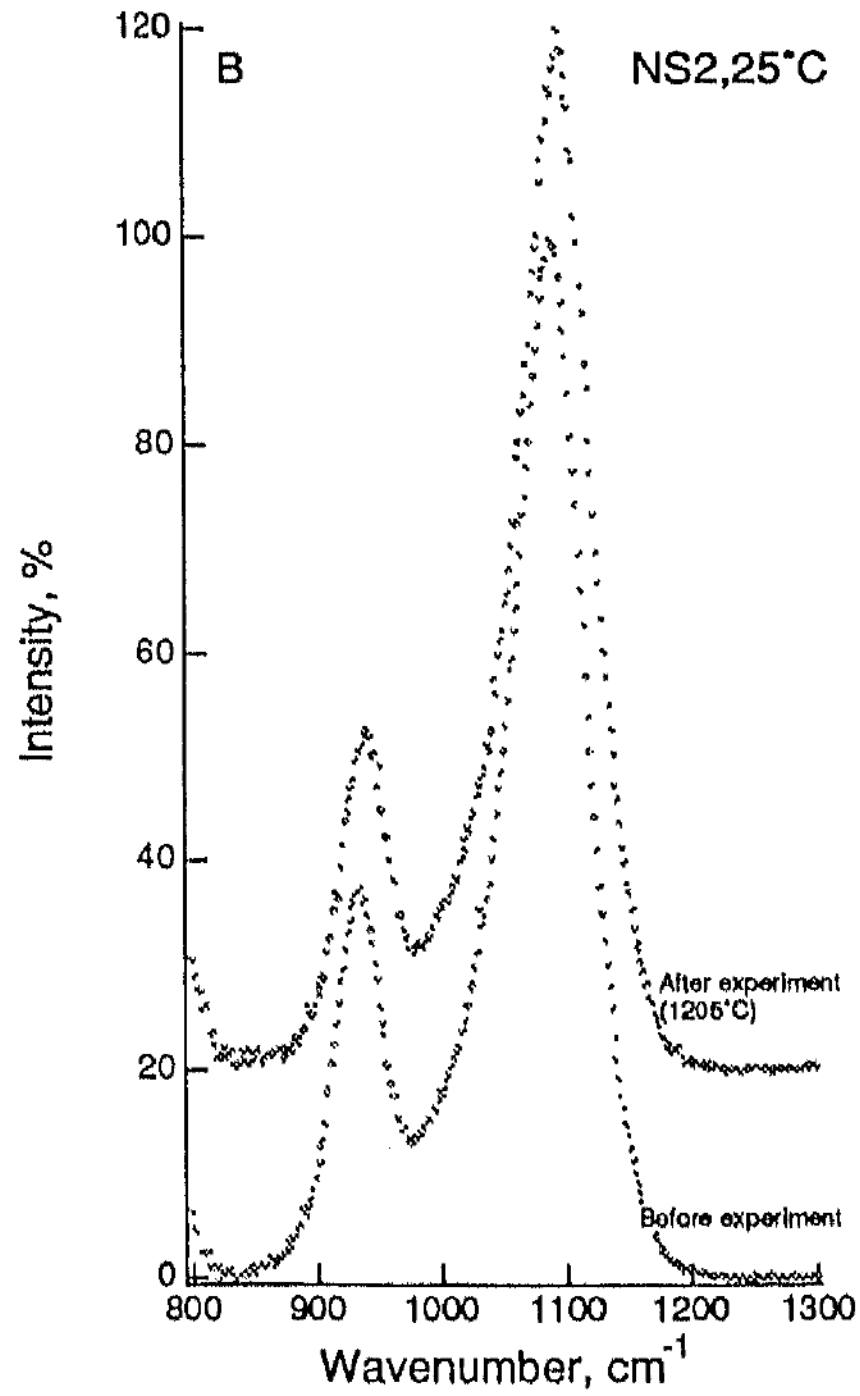
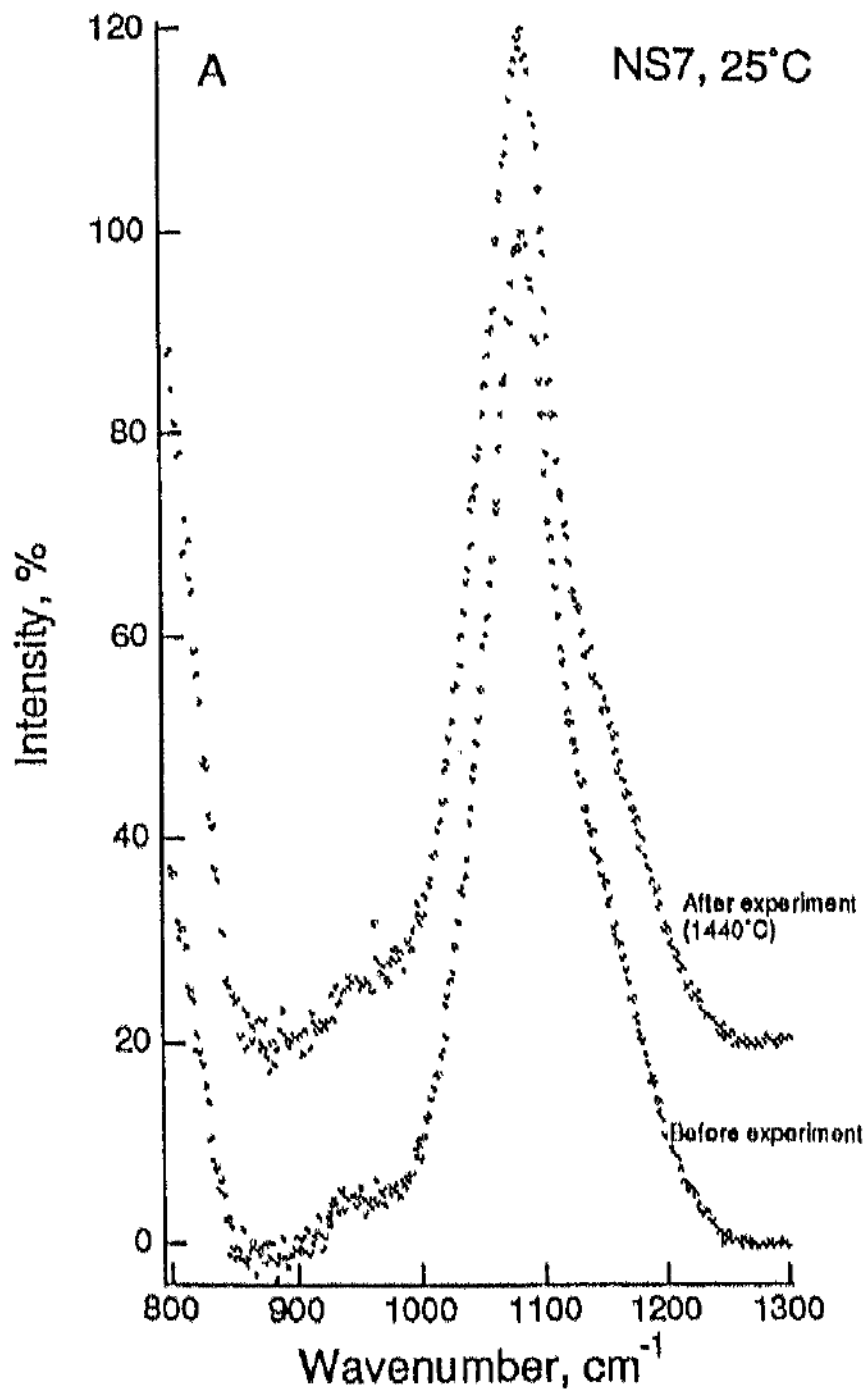
Mysen et Frantz, 1992; Richet et al., 1993; Neuville et Mysen, 1996; Neuville et al., 2008; Ferreira et al., 2013, Neuville et al., 2014

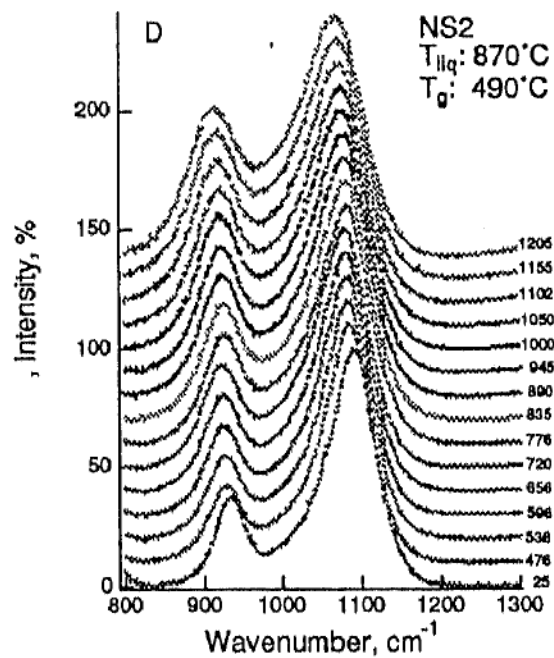
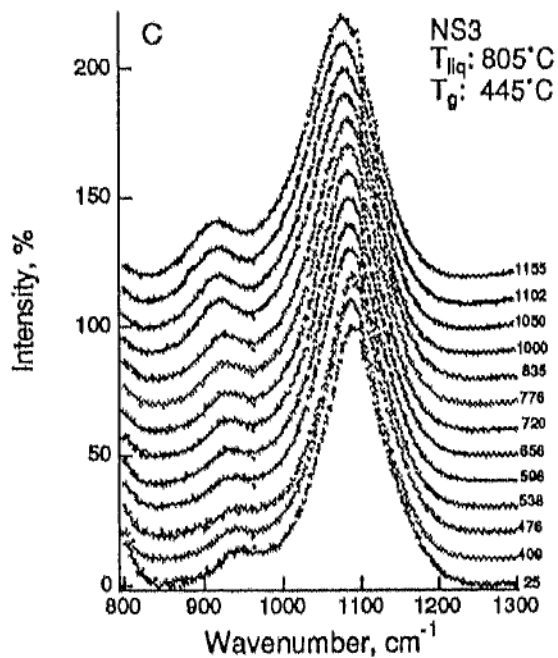
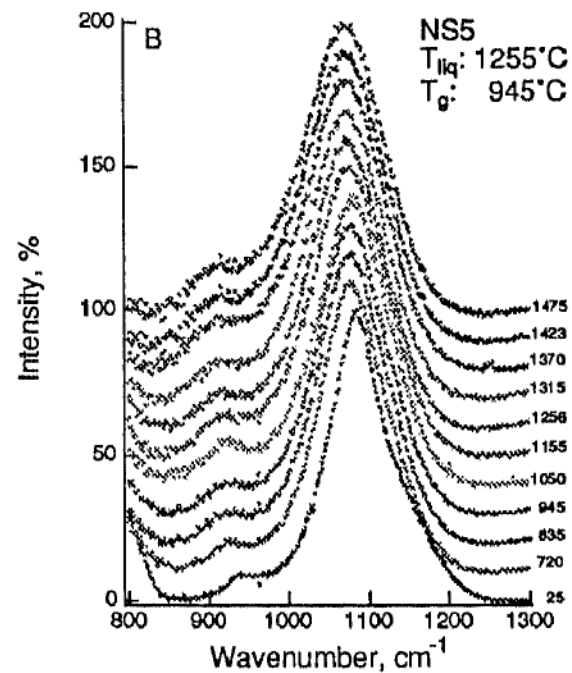
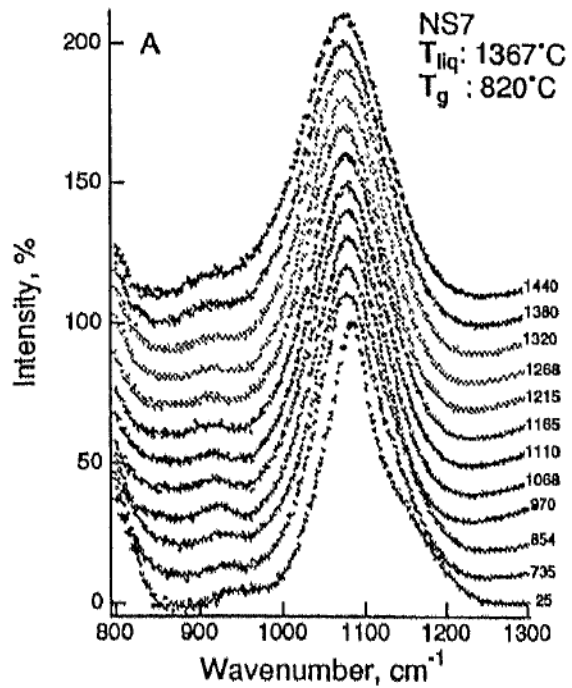
NA65.17

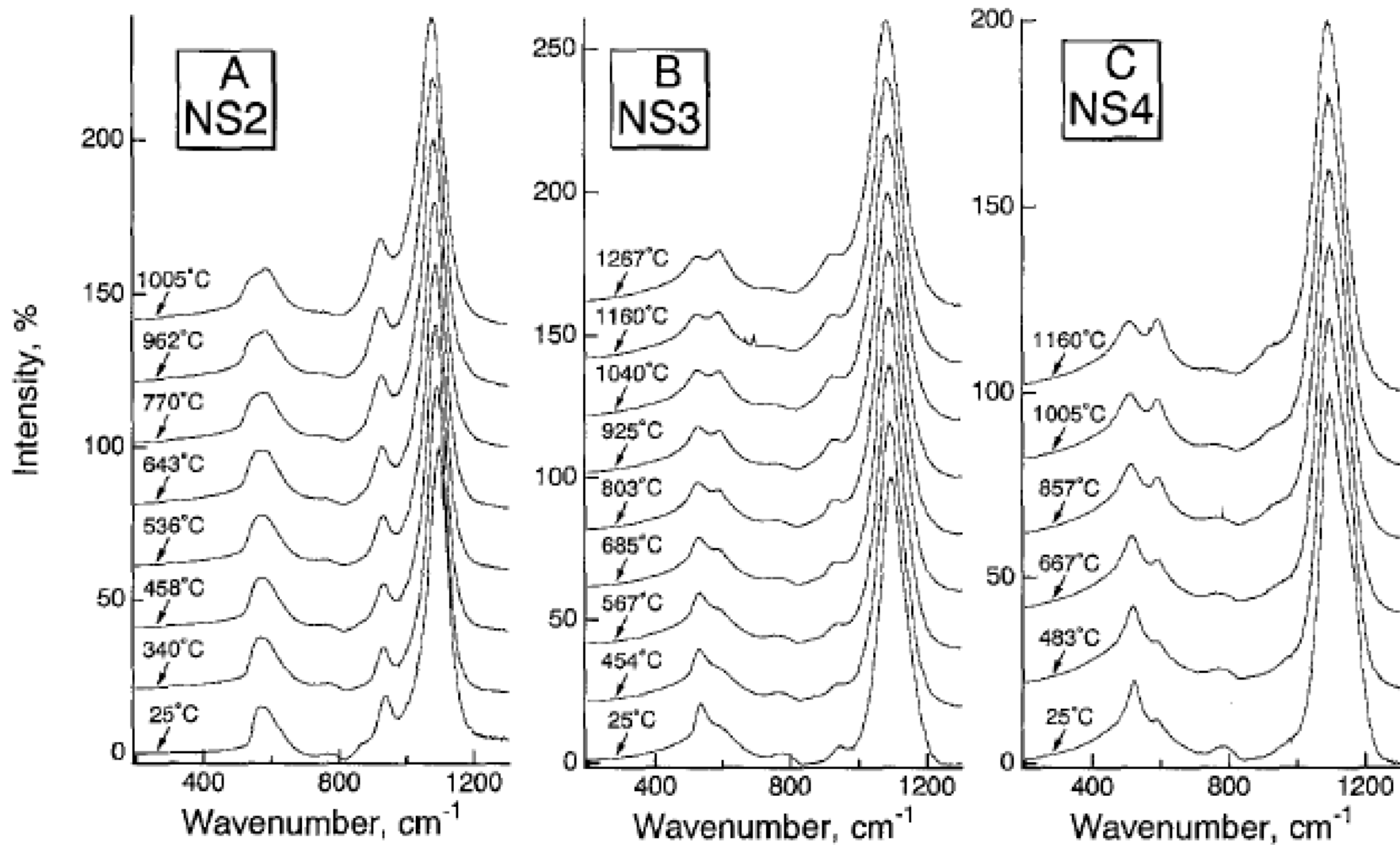
Nécessité de toujours vérifier avant et après
que la composition chimique reste identique

Intensity, %









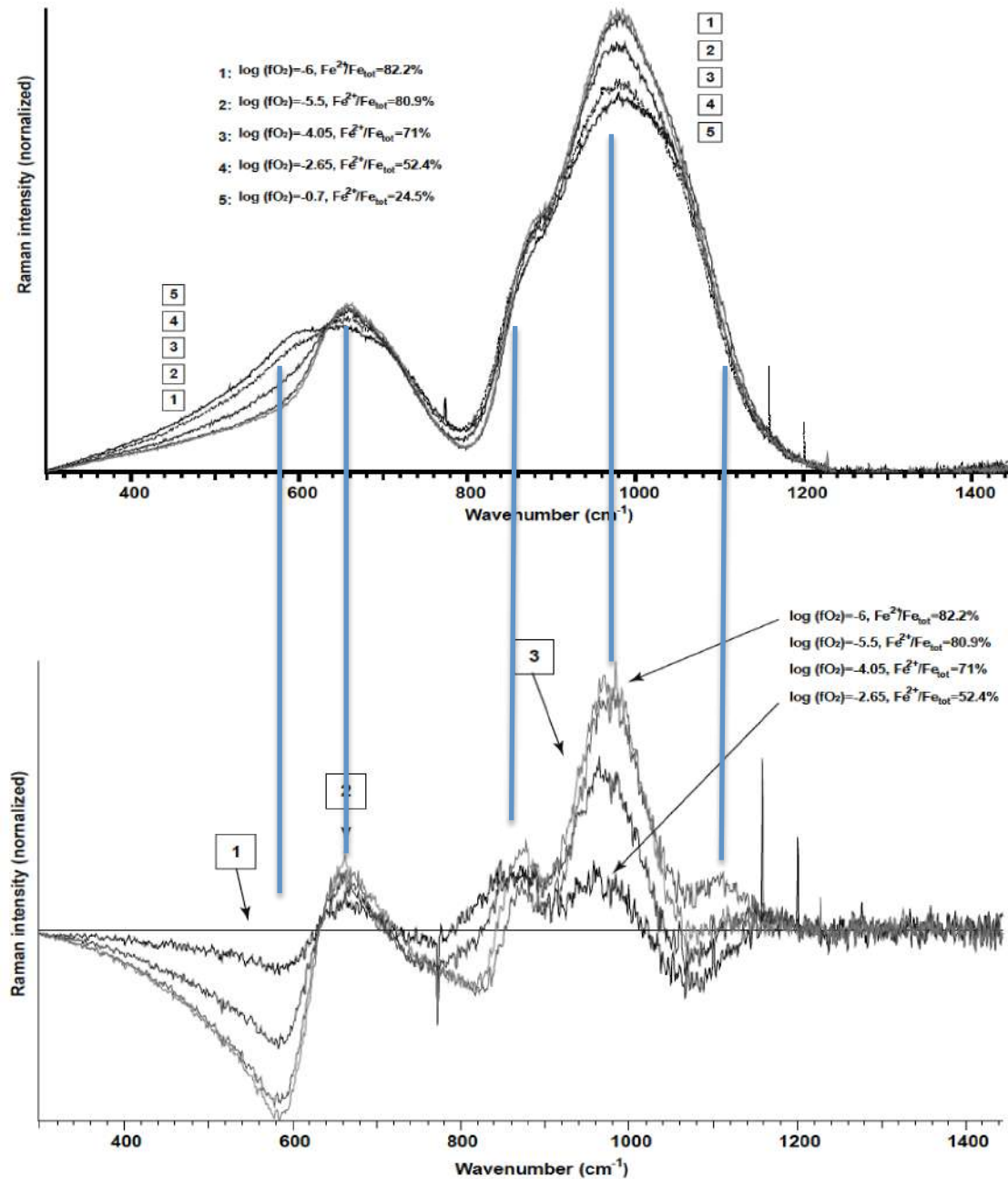
D'autres exemples chez Mysen et al., McMillan, ... Neuville et al., Yano et al.....

Que faire avec un spectre Raman ?

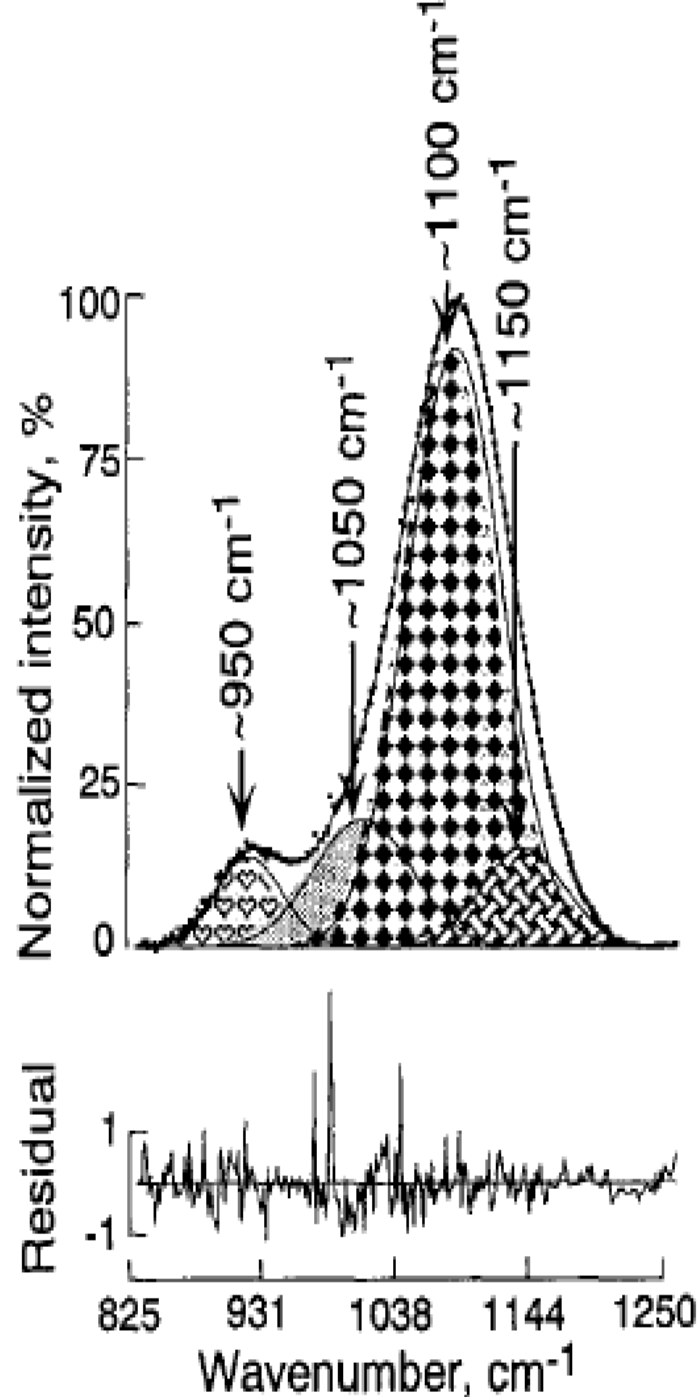
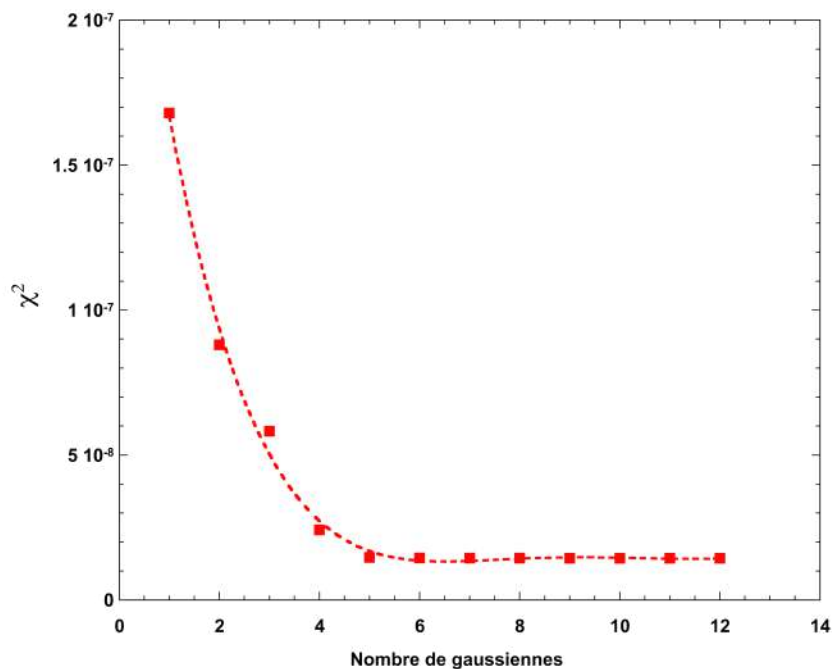
- Analyse et caractérisation de phase
- Reconnaissance et analyse de système
- Potentiellement analyse et décomposition du spectre

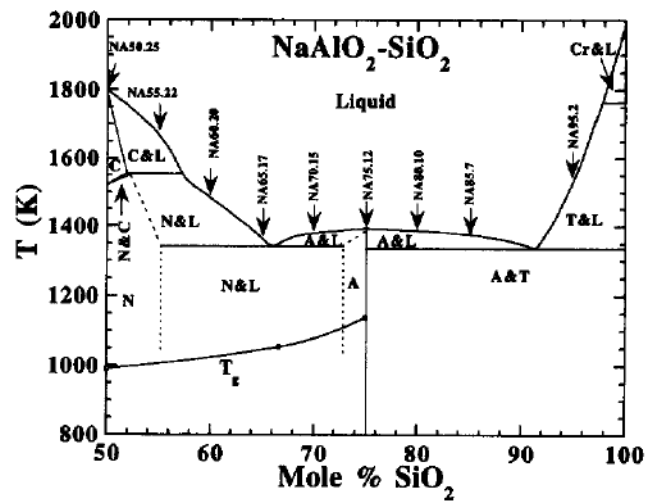
Possibilité de déconvolution en gaussienne dans le cas d'un verre et liquide, lorentzienne pour étudier cristallisation

- Trouver les bandes ?
- Dériver des spectres et chercher point d'inflexion
- Ou faire différence de spectre pour visualiser nouvelles contributions...
- Une fois les bandes définies, laisser le calculs sans contraintes

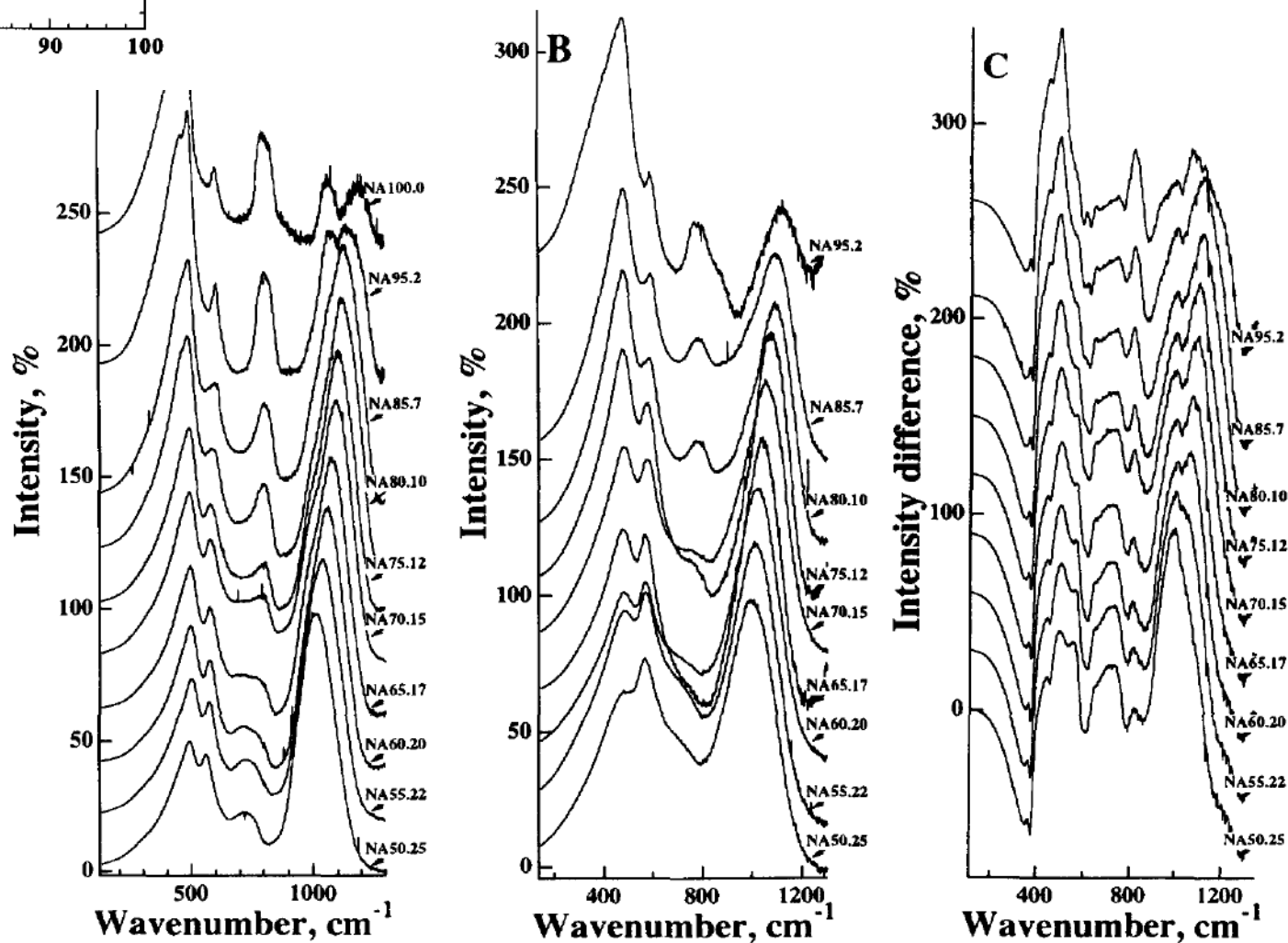


Détermination du nombre de bande en
cherchant le minimum
Mais attention : solution physique et non
mathématiques, parfois préférable une
bande de plus !

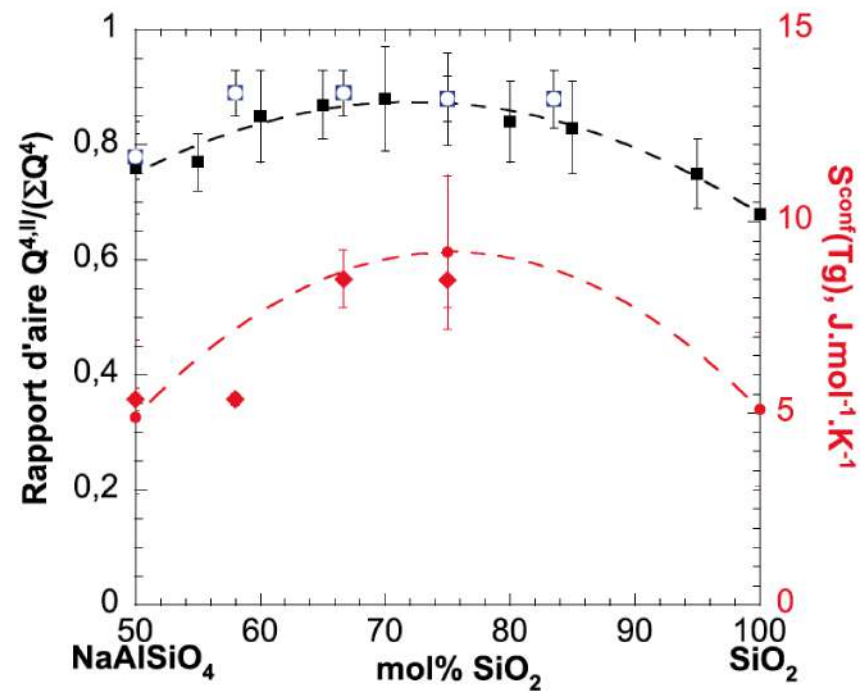
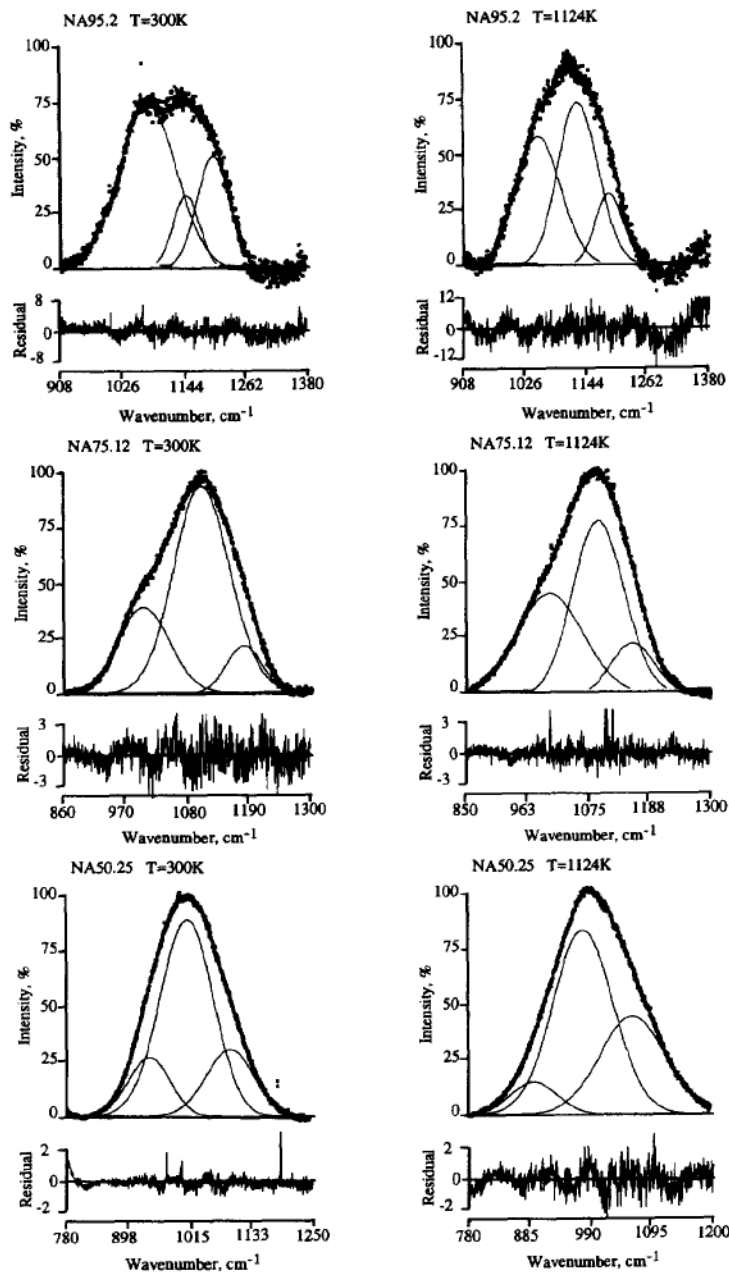




Exemple binaire SiO₂-NaAl₂O₄



Exemple de déconvolution en 3 bandes Q^{4I} , Q^{4II} , T_2 et rapport $Q^{4II}/(Q^{4I}+Q^{4II})$ en fonction $Al/(Al+Si)$

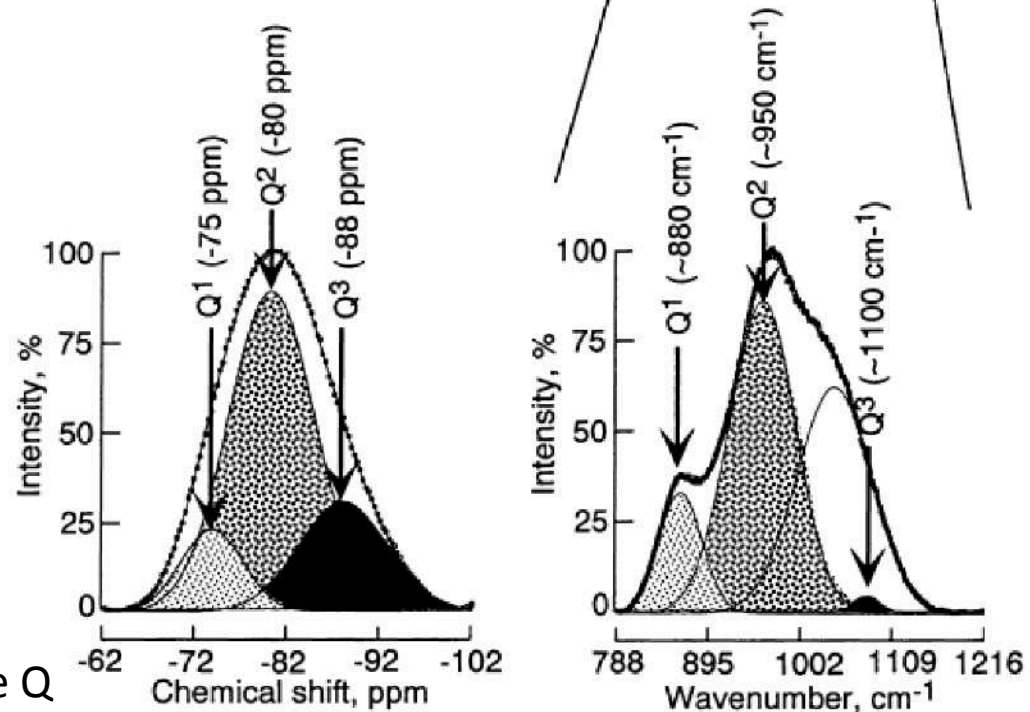
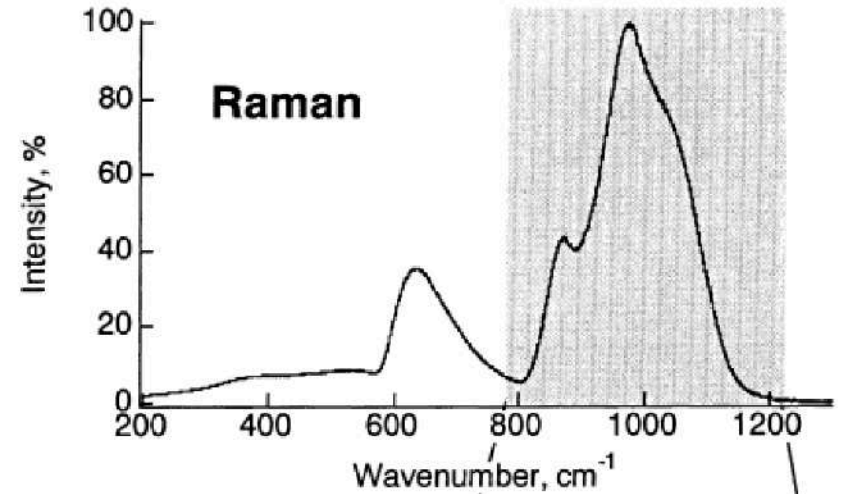
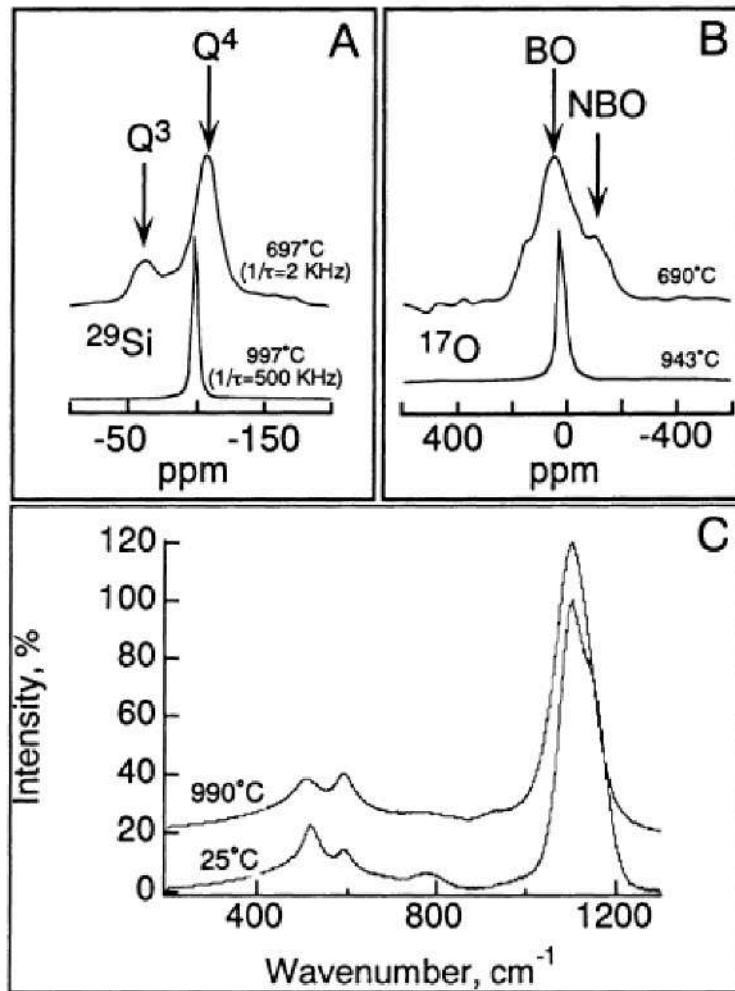


Le Losq (2012) d'après Neuville et Mysen 1996

FIG. 7. Examples of curves-fitted Raman spectra of the compositions at 300 K (room temperature) and 1124 K (closer than the glass transition).

CaSiO₃ glass

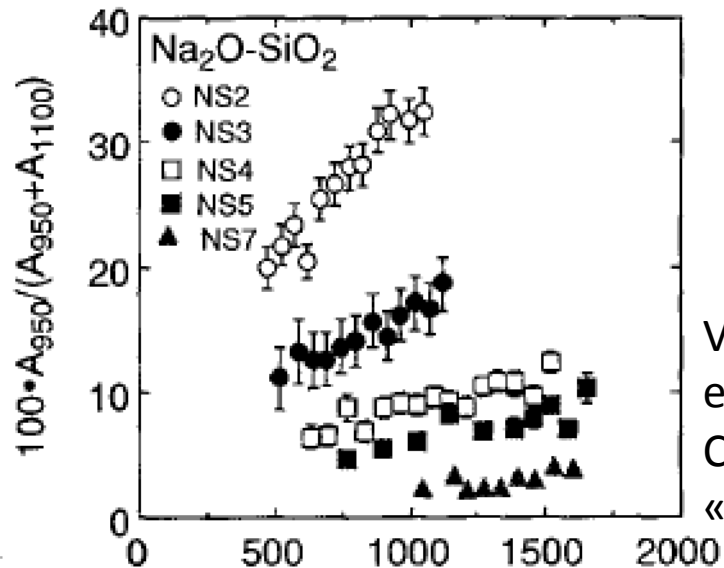
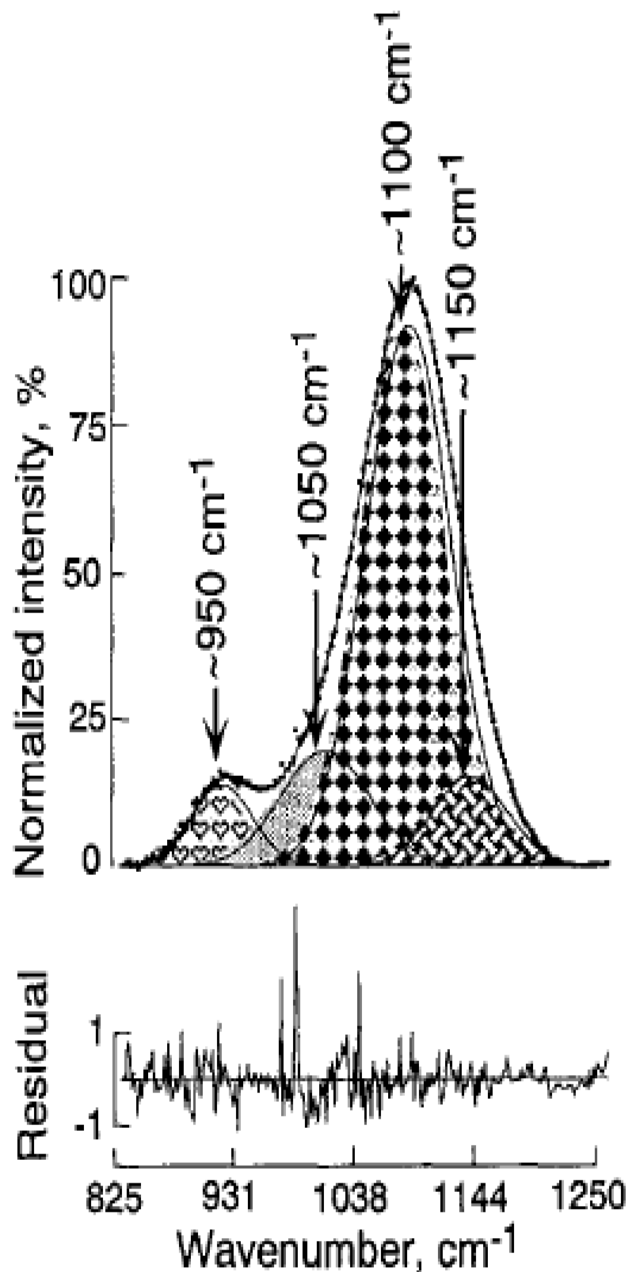
Similude RMN ↔ Raman



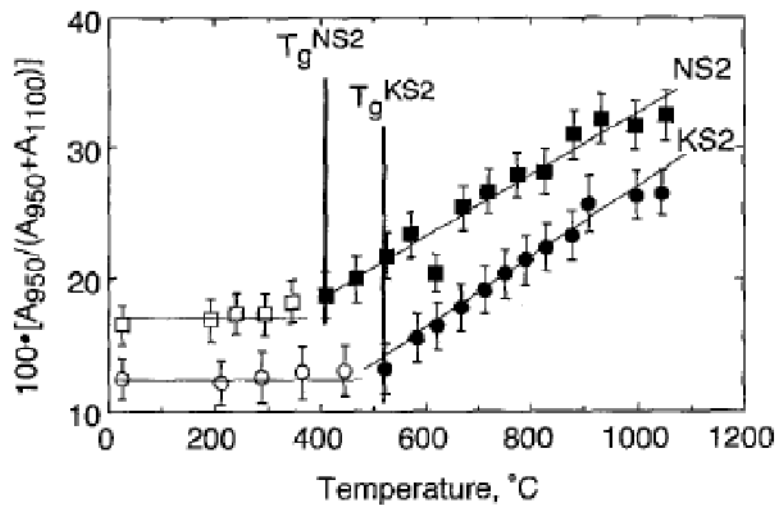
Calcul constante de conversion pour espèce Q

Possibilité de calculer les espèces Q avec le Raman et la calibration

SiO₂ (Q⁴)
Si₂O₅ (Q³)
SiO₃ (Q²)

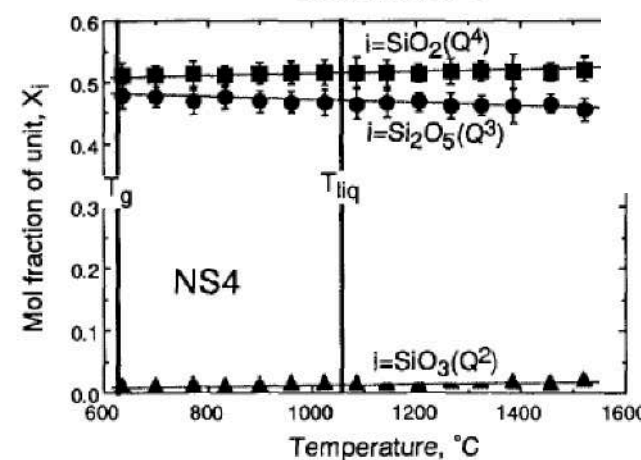
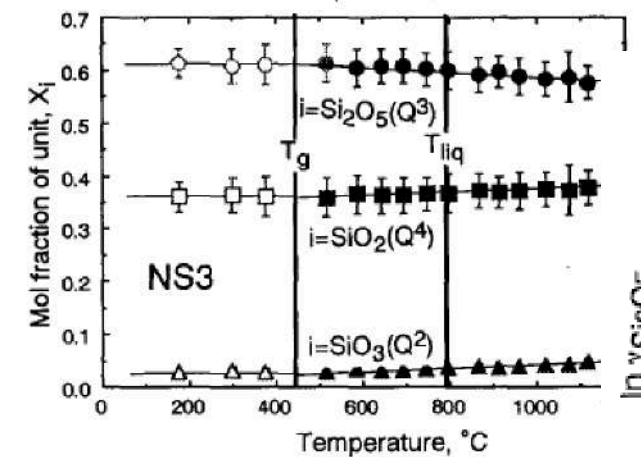
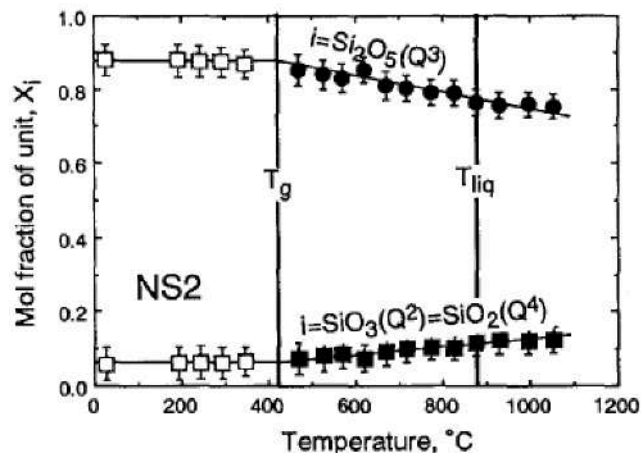


Variation des espèces Q
 en fonction de T
 Calcul de constante
 « thermodynamiques



$$K_x = \frac{X_{Q^2} \cdot X_{Q^4}}{(X_{Q^3})^2}$$

Mysen et Frantz, 1992, 1993, 1995...

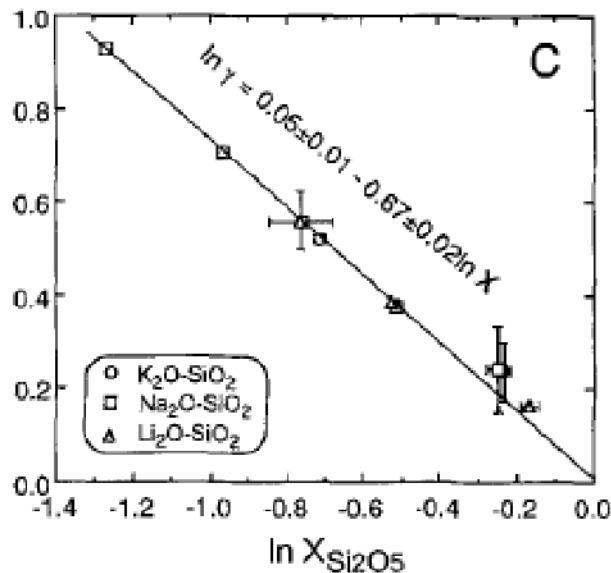


$$K = aSiO_3aSiO_2aSi_2O_5. (3)$$

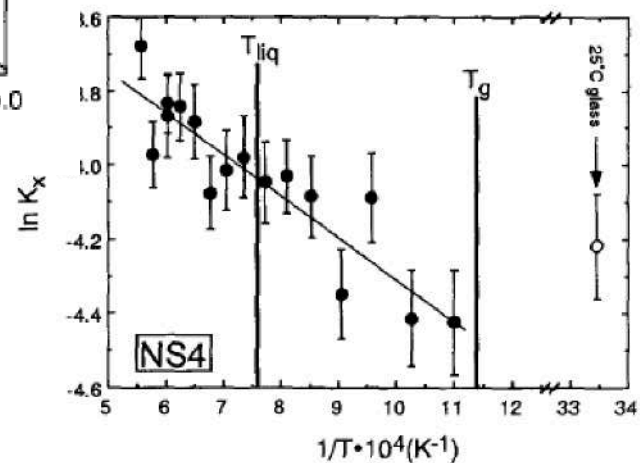
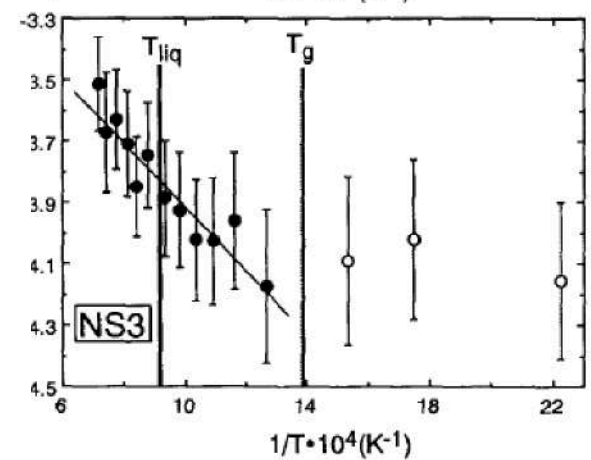
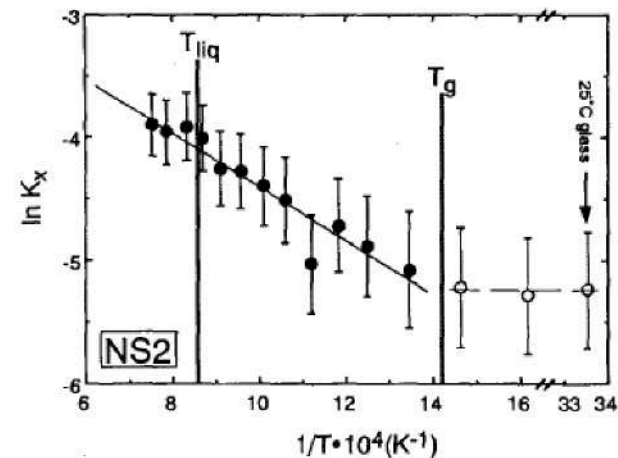
$$K_x = X_{SiO_3}X_{SiO_2}/X_{Si_2O_5}.$$

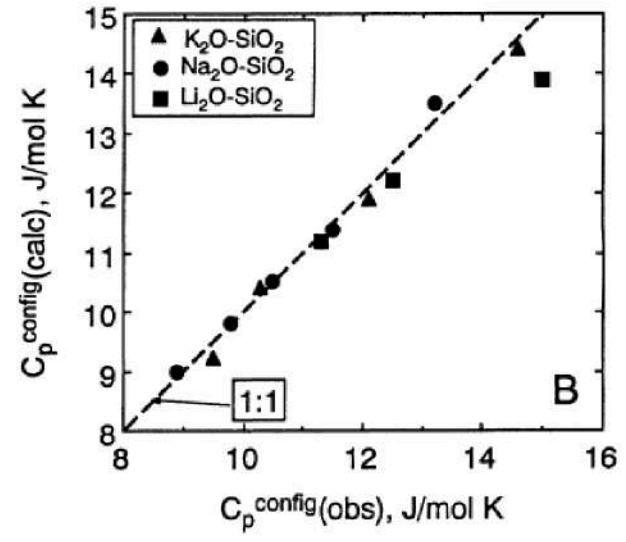
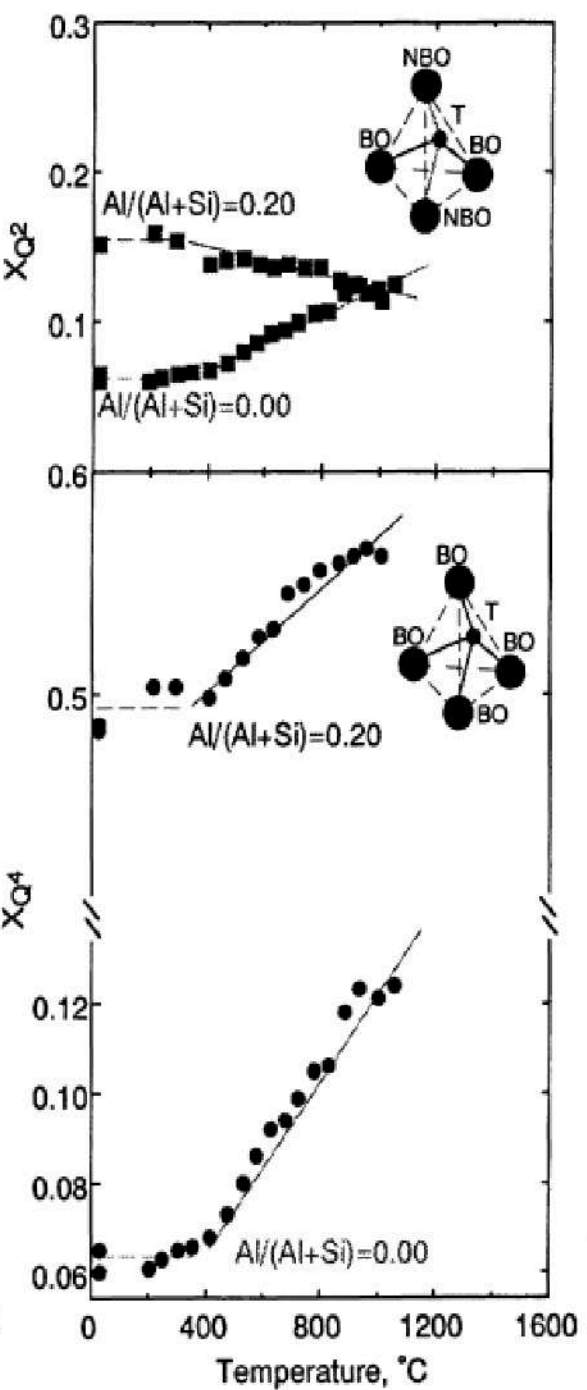
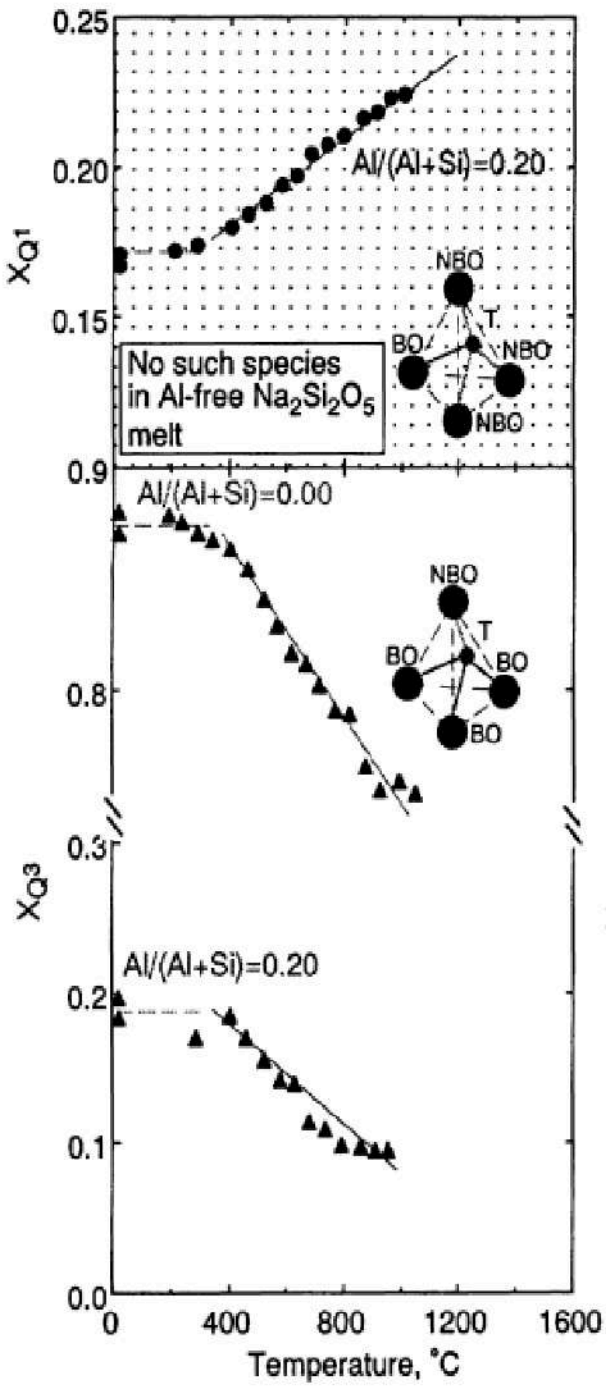
$$\delta \ln K_x / [\delta(1/T)] = -\Delta H/R.$$

$$K_x = a/T + b$$



Possibilité de calcul de
grandeur réactionnelle





Mysen arrive à recalculer les chaleurs spécifiques de configuration

$$S^{conf}(Tg) = -R[x_{Q^{4,II}} \ln(x_{Q^{4,II}}) + x_{Q^{4,I}} \ln(x_{Q^{4,I}}) + x_{Si-O-Si} \ln(x_{Si-O-Si}) + x_{Si-O-Al} \ln(x_{Si-O-Al})].$$

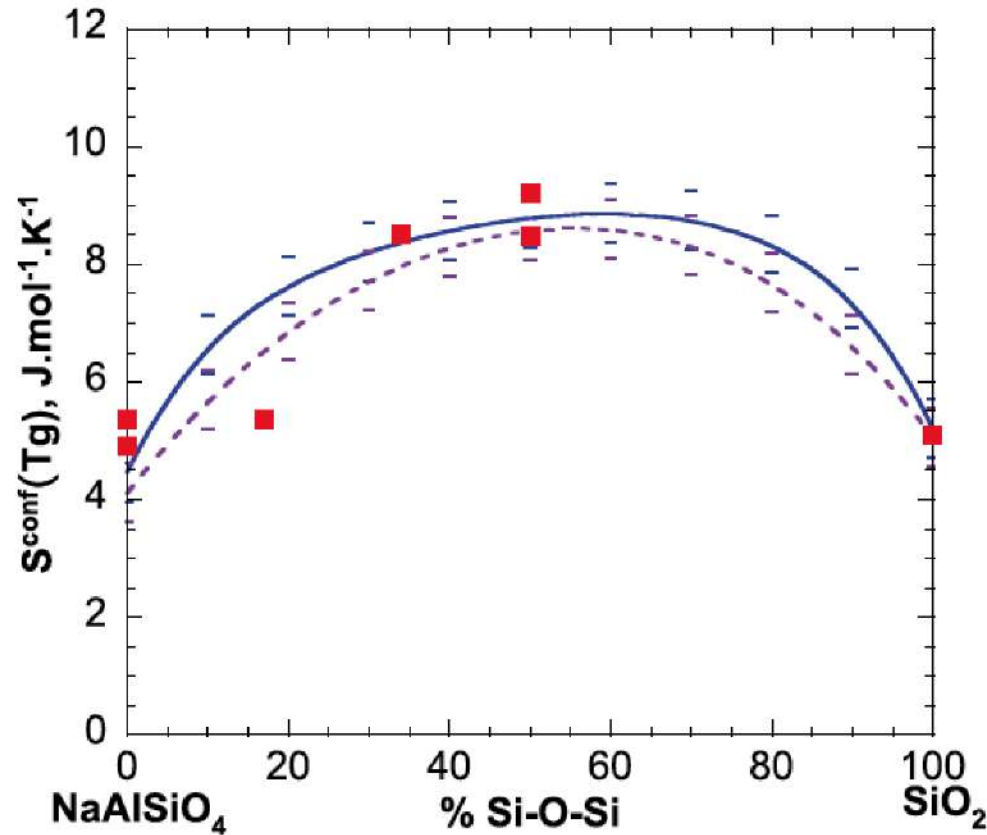
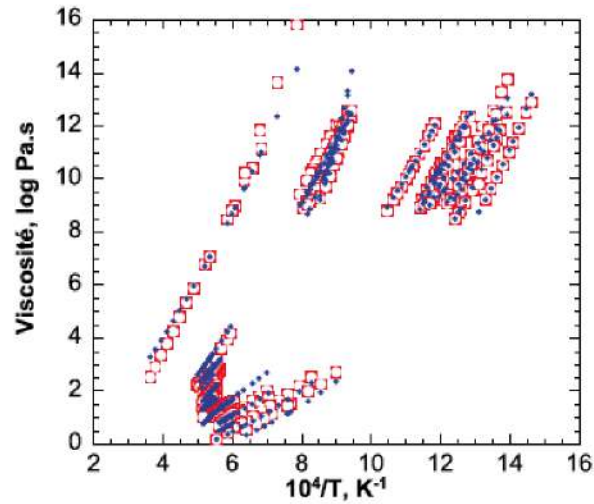
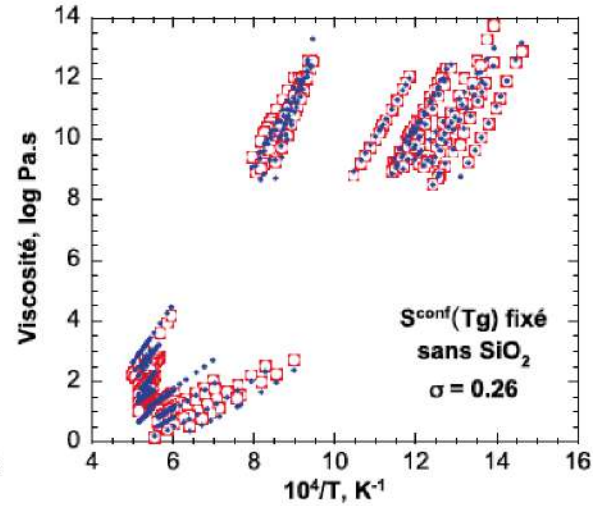


FIGURE 7.3: Entropie de configuration à Tg en fonction de la proportion molaire de liaisons Si-O-Si le long du joint 1 du diagramme NAS. Les valeurs de $S^{conf}(Tg)$ déterminées à l'aide des mesures de viscosité et de capacité calorifiques sont les carrés rouges. Les valeurs données par les modèles des équations 7.6 et 7.7 sont respectivement les courbes en bleu et violet. Les pointillés représentent les barres d'erreurs inférieures et supérieures des modèles.

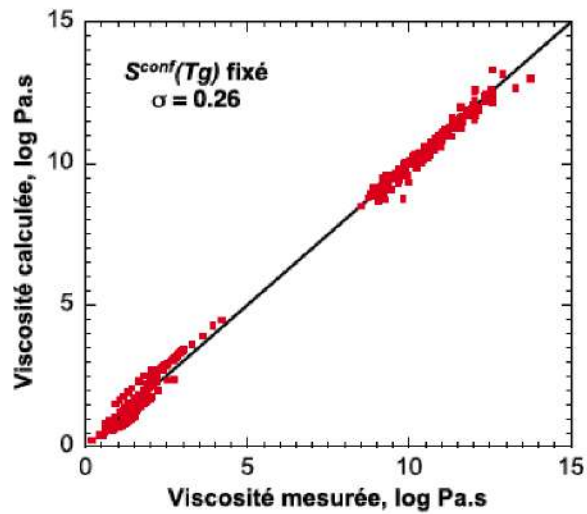
Calcul des viscosités à partir d'une modélisation des espèces Q, Le Losq et ., 2013



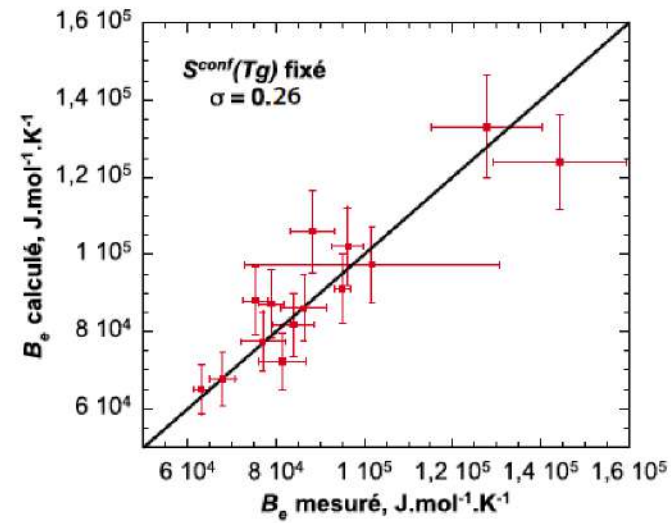
(a)



(b)



(c)



(d)

Ça marche !

Temperature-Induced Structural Modifications Between Alkali Borate Glasses and Melts

L. Cormier,^{*,†,‡} O. Majerus,^{‡,§} D. R. Neuville,[¶] and G. Calas^{*,‡}

Détermination rapport BO₄ / (BO₃+BO₄) en fonction de T...

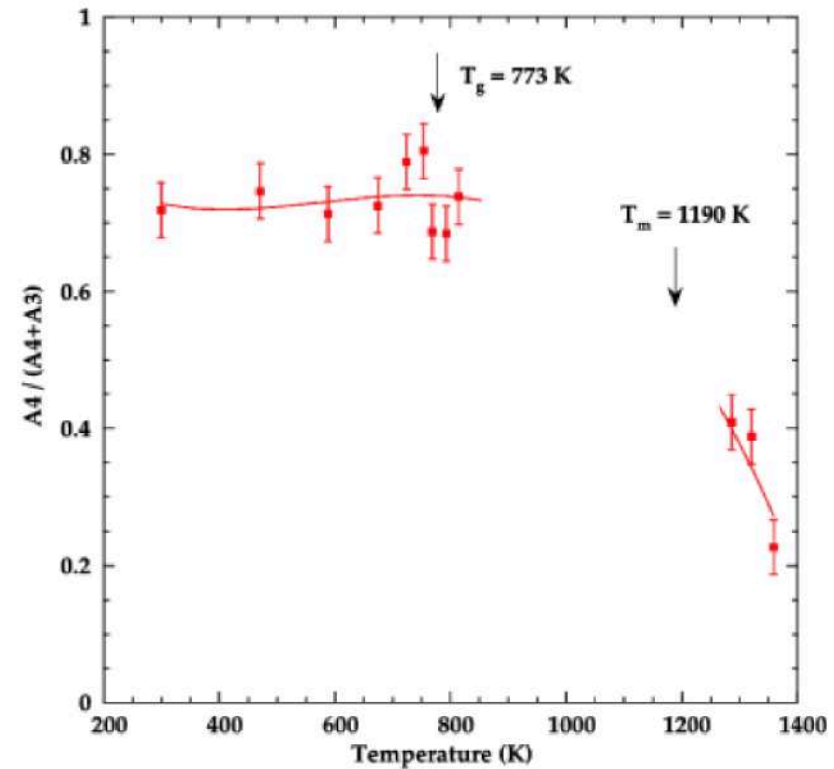
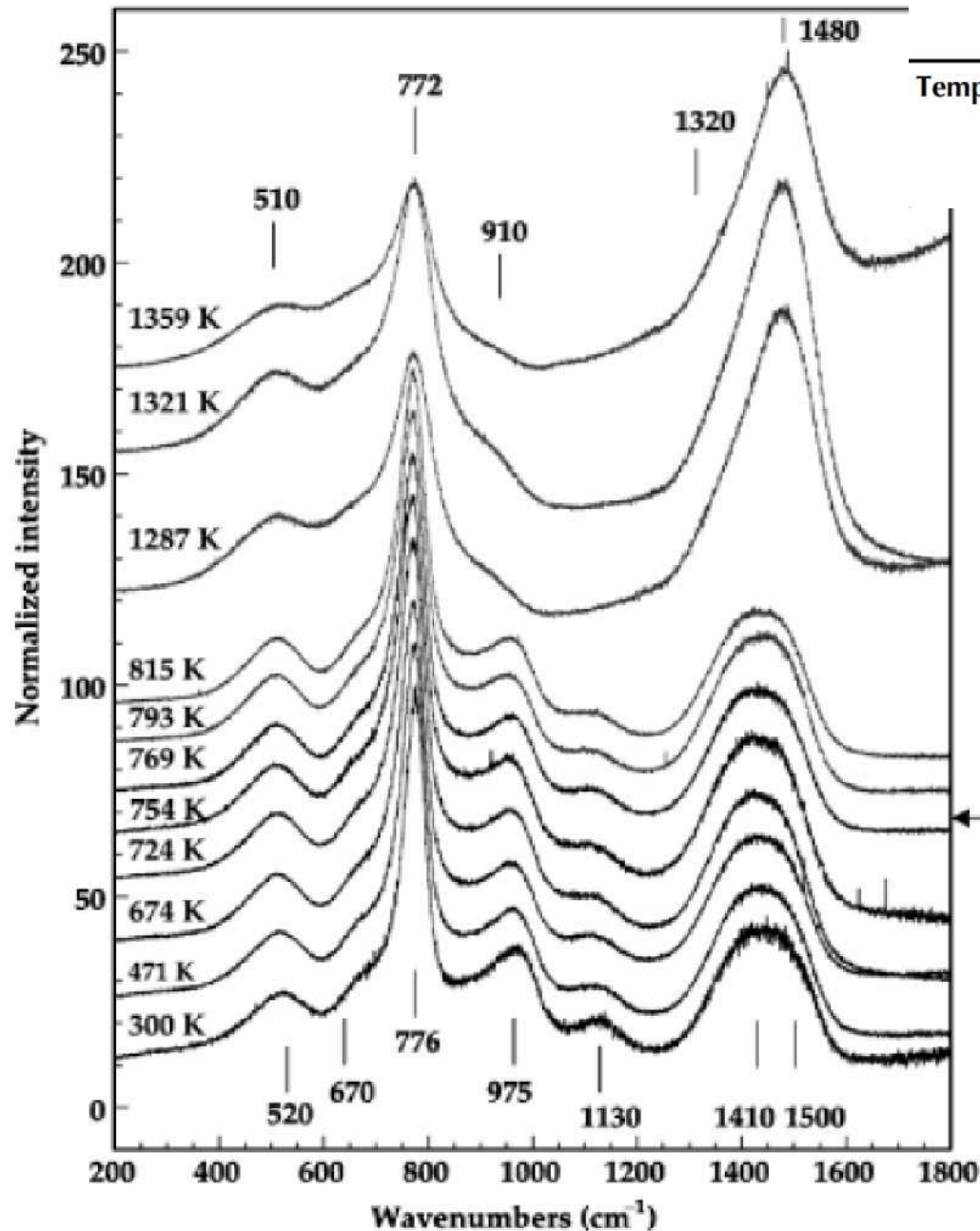
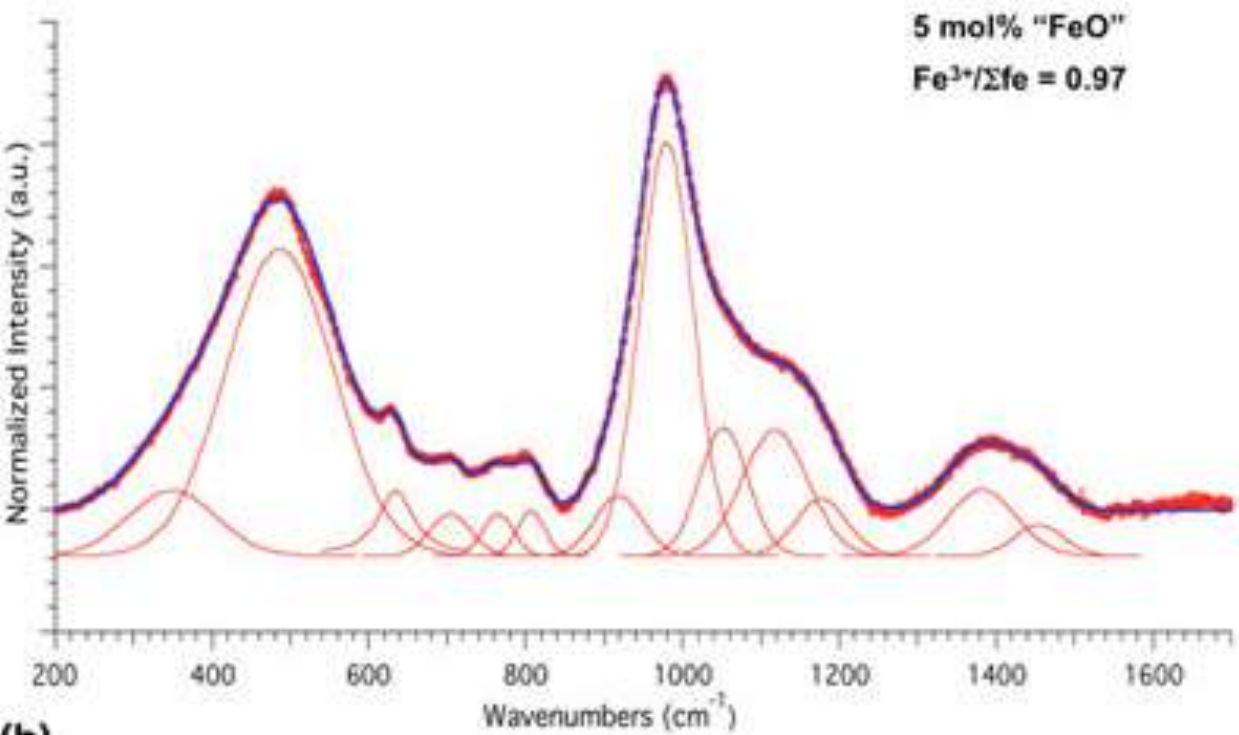
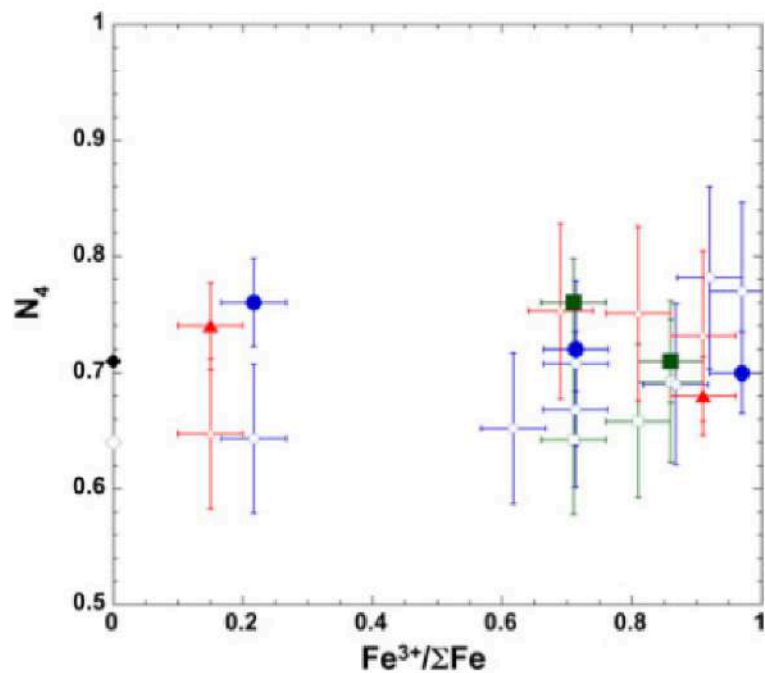


Fig. 3. Raman spectra for the 6LB2 glass from room temperature to 1359 K. The glass transition temperature (T_g) is indicated.

En partie faux car sous estimation des BO₄ mais....



A ₁	—
A ₂	—
A ₆₃₀	Danburite
A ₇₀₀	Metaborate (BO ₃)
A ₇₇₀	Pentaborate (BO ₄)
A ₈₀₃	Boroxols (BO ₃)
A ₉₃₀	Pentaborate (BO ₄)
A ₉₈₀	Fe ³⁺
A ₁₀₆₀	M
A ₁₁₂₀	Q ⁴
A ₁₁₇₅	Q ⁴
A ₁₃₈₀	BO ₂ O ⁻ -BO ₄
A ₁₄₅₀	BO ₂ O ⁻ -BO ₃
AR (Fe ³⁺)	
N _{4R}	

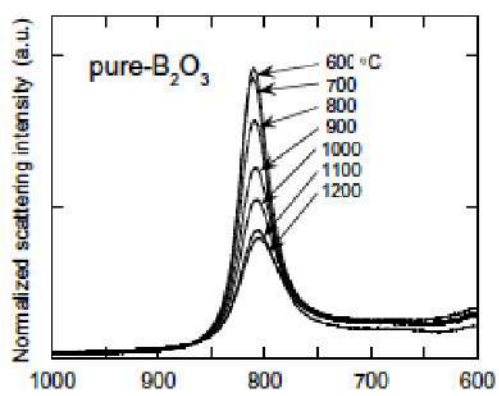


Vrai rapport

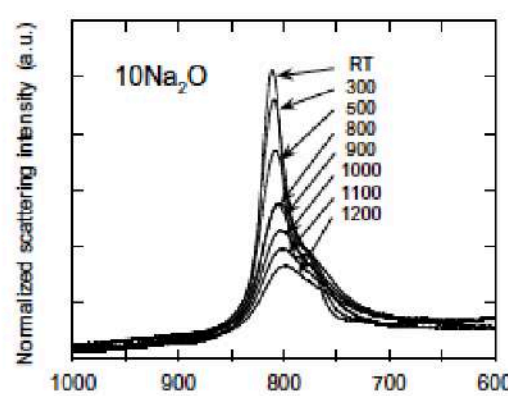
$$N_4 = \frac{\Sigma BO_4}{(\Sigma BO_4 + \Sigma BO_3)}$$

Possibilité de suivre N₄ en fonction de X et T

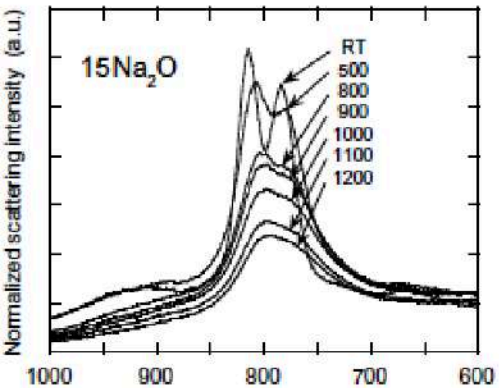
Yano, 2003, JNCS



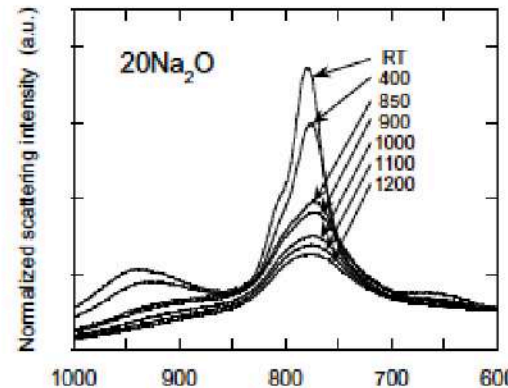
(a) Raman shift (cm⁻¹)



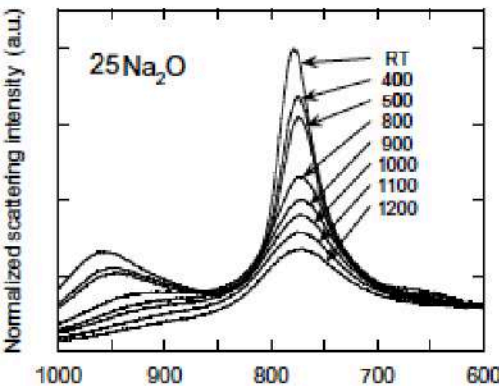
(b) Raman shift (cm⁻¹)



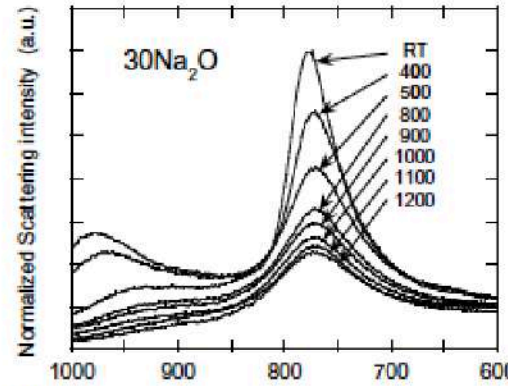
(c) Raman shift (cm⁻¹)



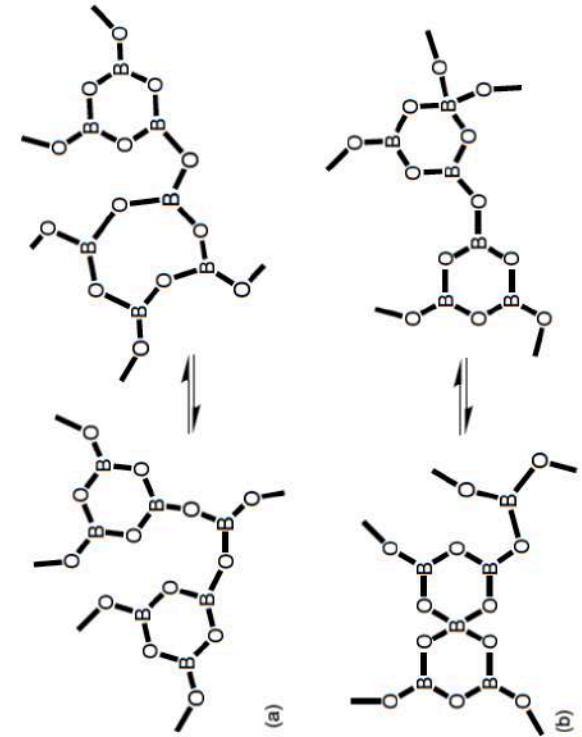
(d) Raman shift (cm⁻¹)



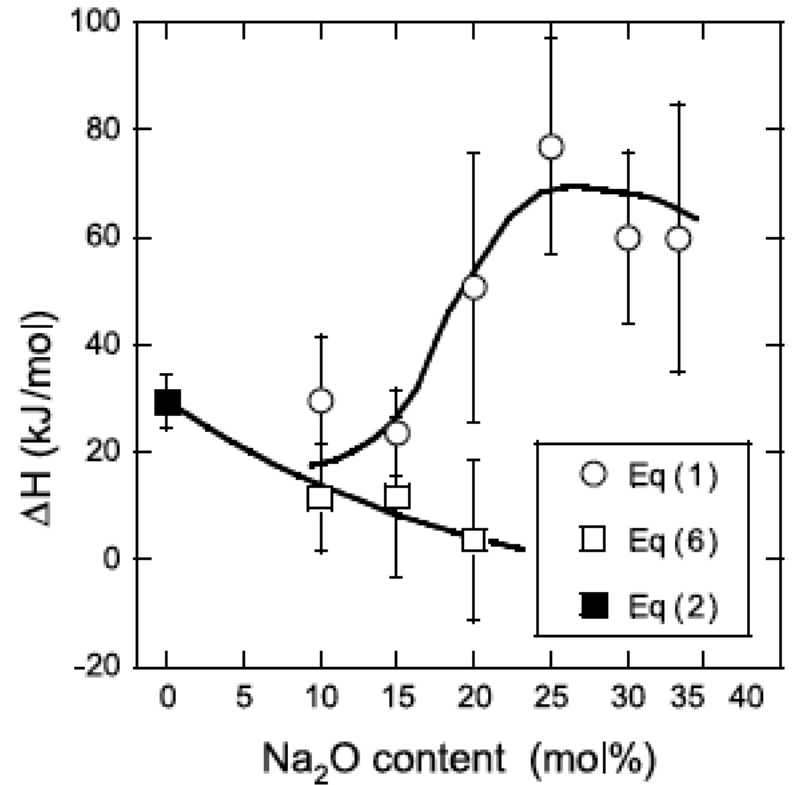
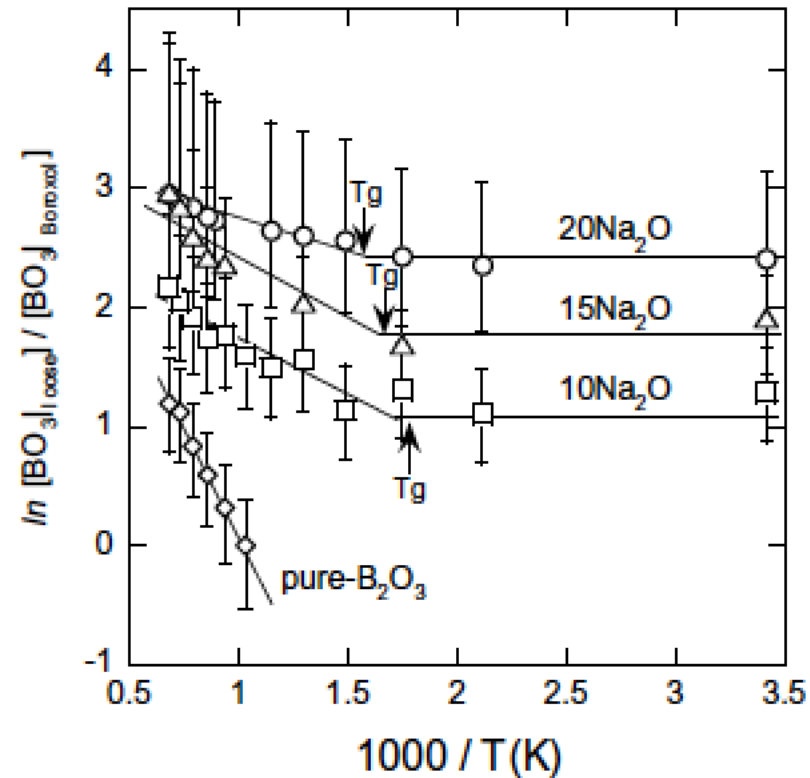
(e) Raman shift (cm⁻¹)



(f) Raman shift (cm⁻¹)



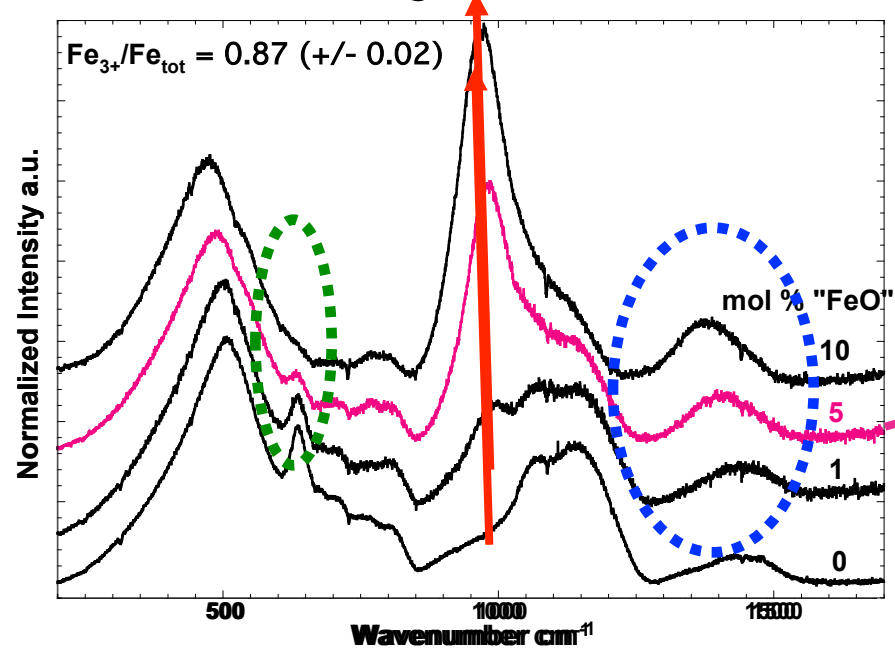
Calcul d'espèces Q ou d'arrangements tétraédriques



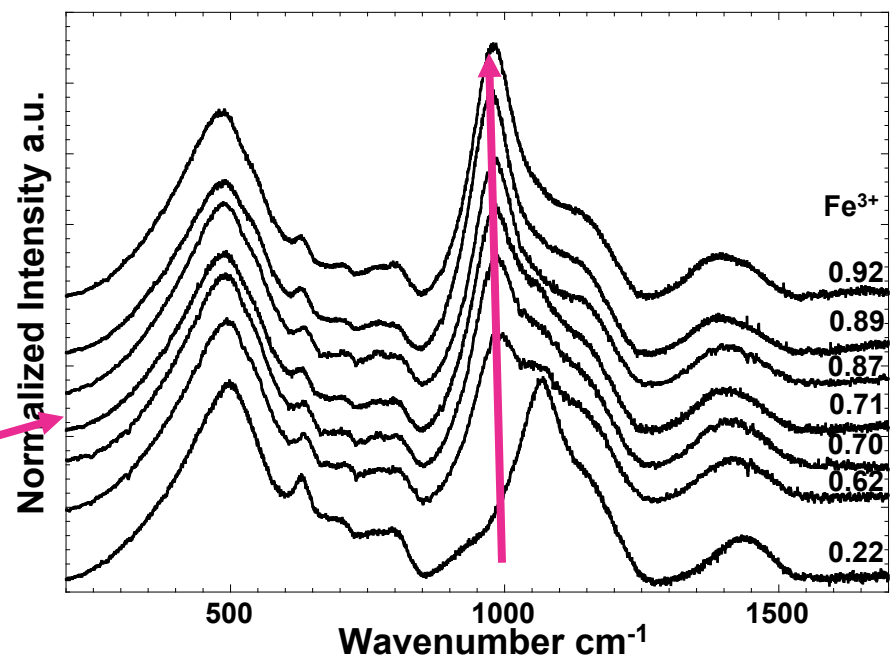
Yano propose des calculs de ΔH en se basant sur BO₃ et BO₄ à haute fréquence uniquement

Rédox en T

Borosilicate NBF67.18.x glass with increasing FeO content



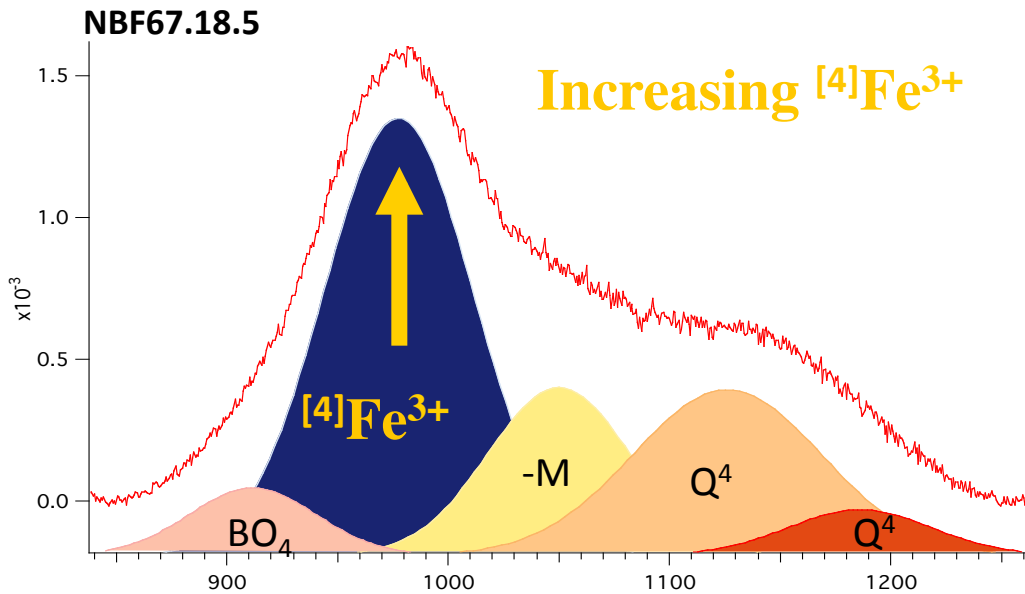
Borosilicate NBF67.18.5 glass with increasing Fe³⁺ content



Increasing FeO content at constant redox ratio + inscreasing Fe³⁺ content:

- Increasing band at 980cm⁻¹ in borosilicates
- Shift to lower frequency of the 980 cm⁻¹ band => [4]Fe³⁺-O bonds shared with Si
- BO₃/BO₄ modification
- Decreasing danburite like rings band (*2SiO₂-2BO₄-Na₂O*)

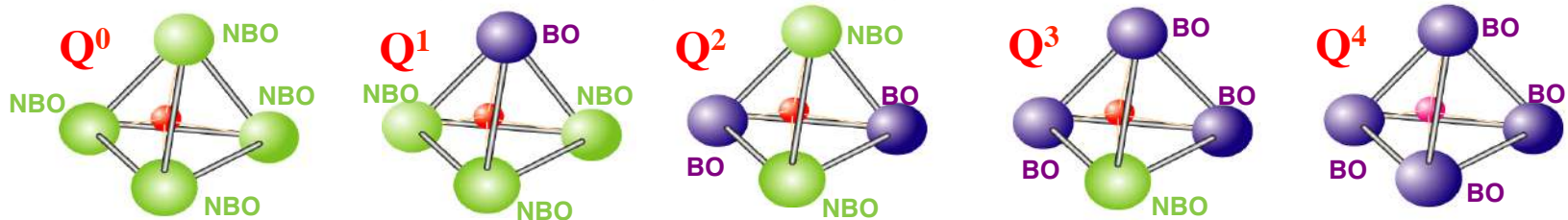
Calibration of the Raman spectroscopy



Evidence of Fe^{3+} in tetrahedral coordination in Q^4 :

- Mössbauer => center shift < 0.30mm/s (Alberto et al. 1996; Rossano et al. 1999)
- Iron K -edge XANES => integrated pre-edge area characteristic for $[4]Fe^{3+}$ (Galoisy et al, 2001; Wilke et al. 2005, 2007)

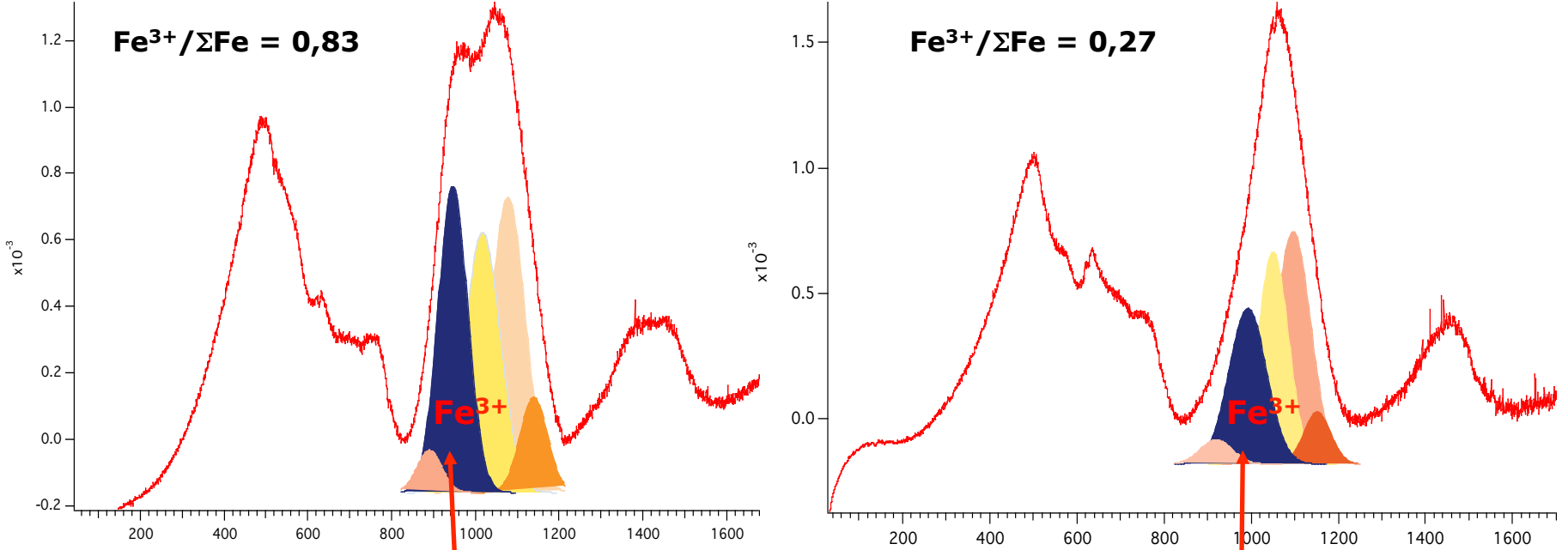
Bands of Q^n species (Q = Si, Al)



Cochain et al. (2012)

Proportion of diverse structural entities:

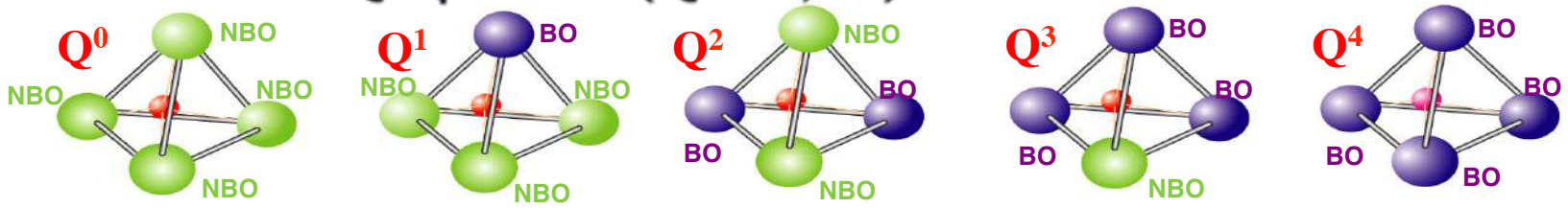
Area ratio of individual bands (Mysen et al., 1892; Mysen et al., 1984)

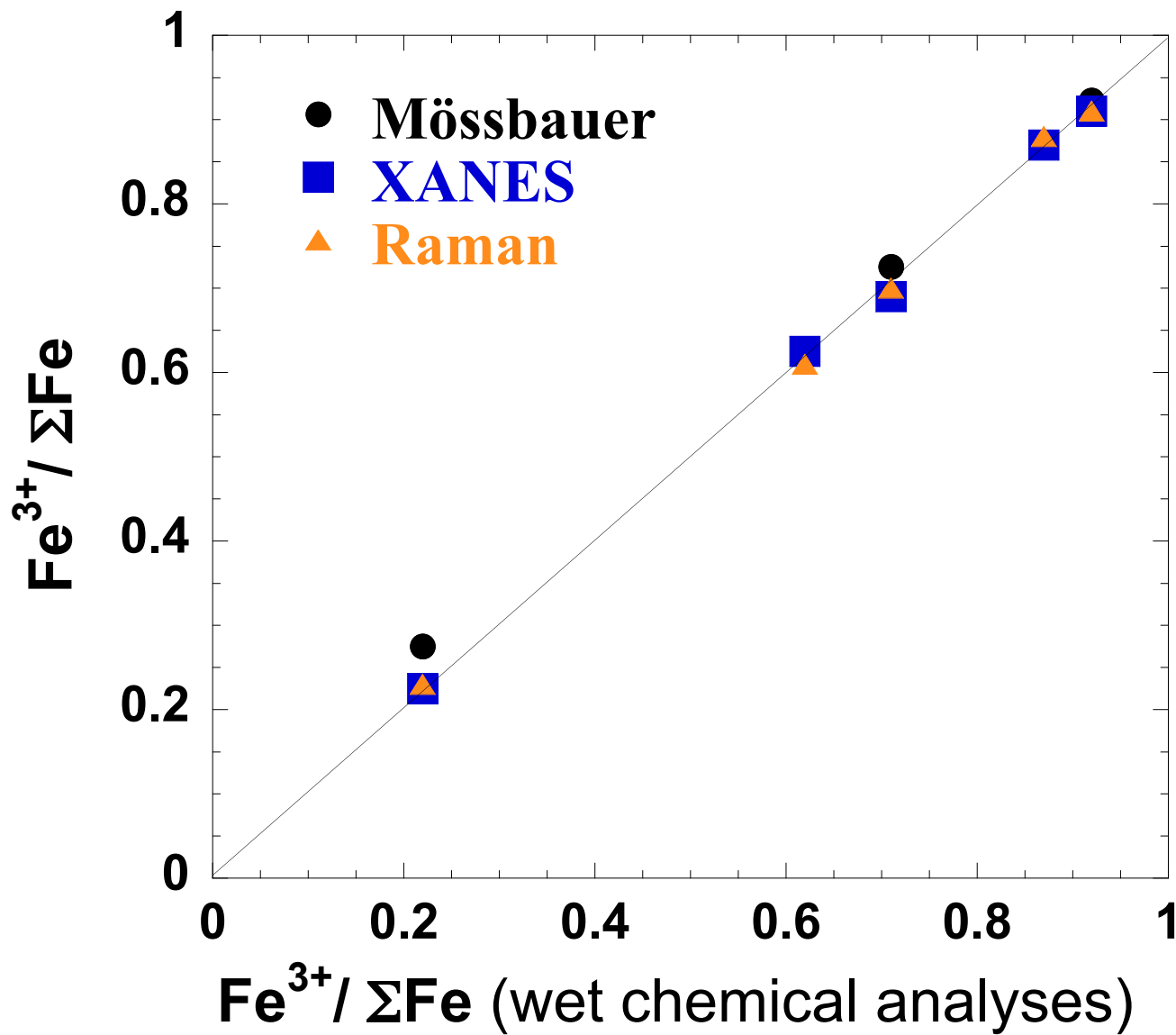


Borosilicate glasses in two different redox states

$$Fe^{3+} / \Sigma Fe = A(Fe^{3+}) / \Sigma A$$

Bands of Q^n species (Q = Si, Al)

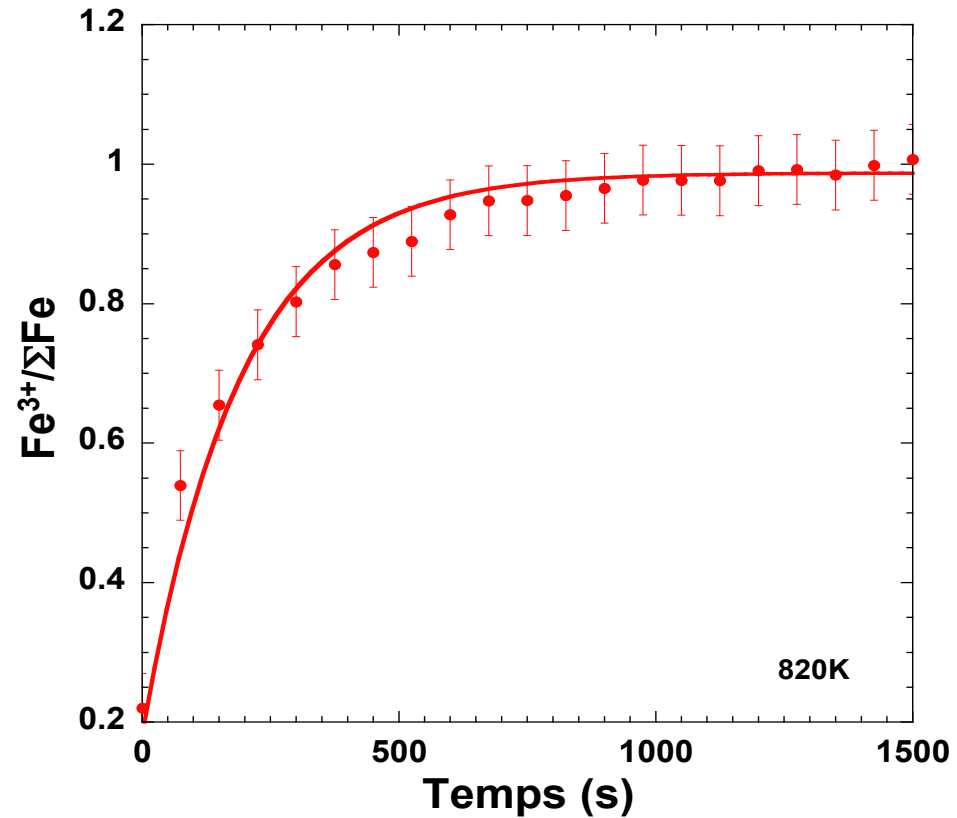
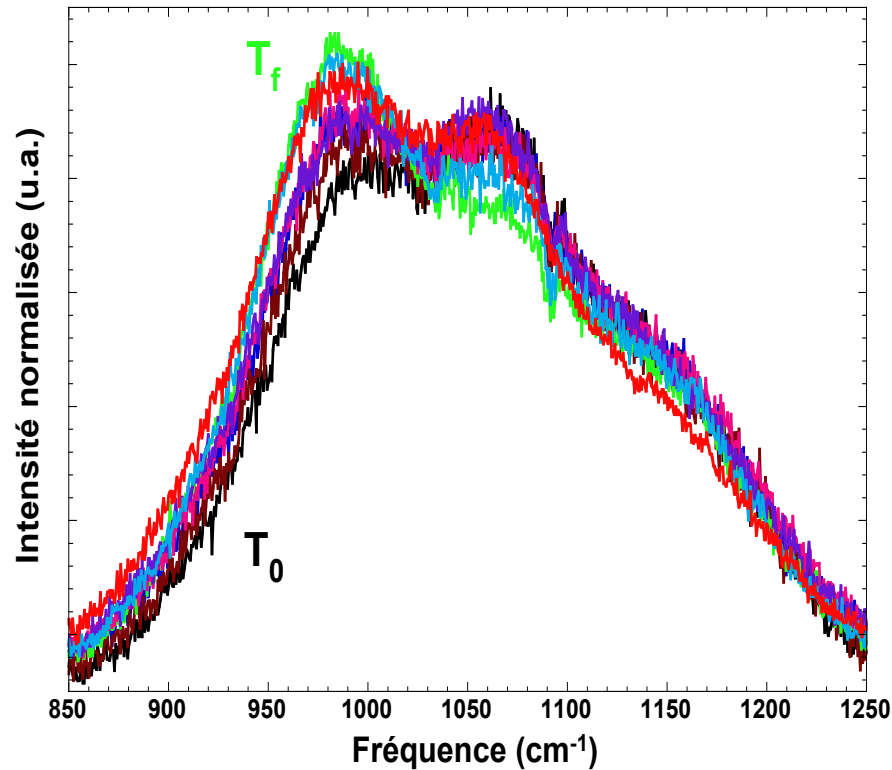




=> Good compatibility between different techniques

Magnien et al., 2006

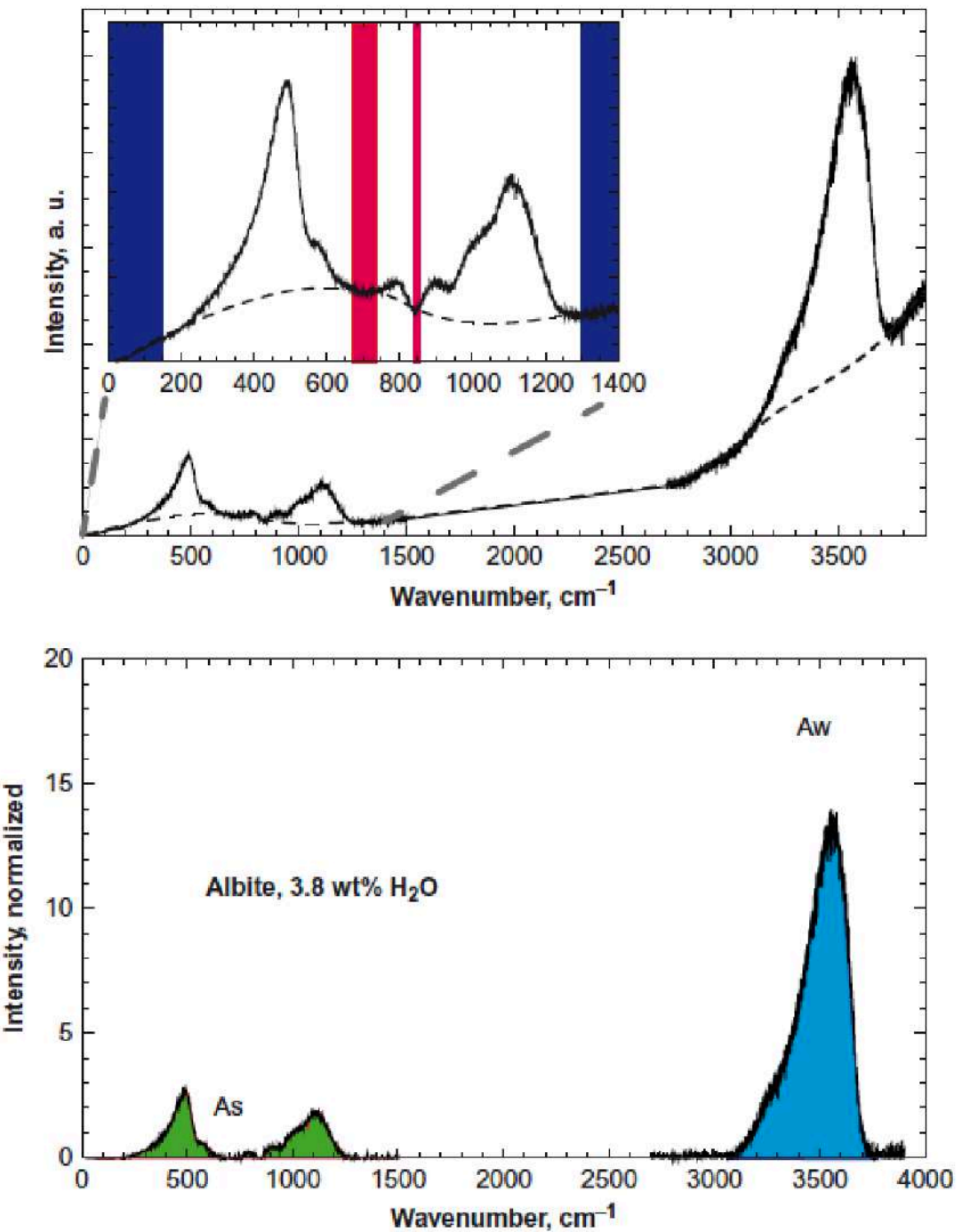
Évolution en T du rapport rédox

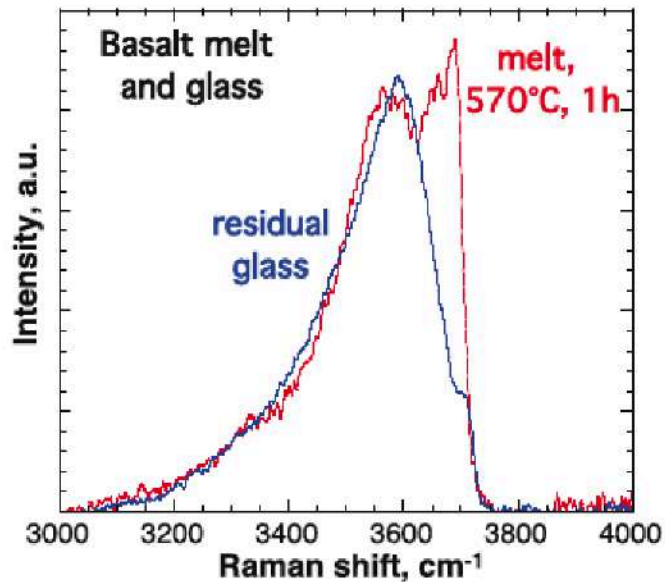
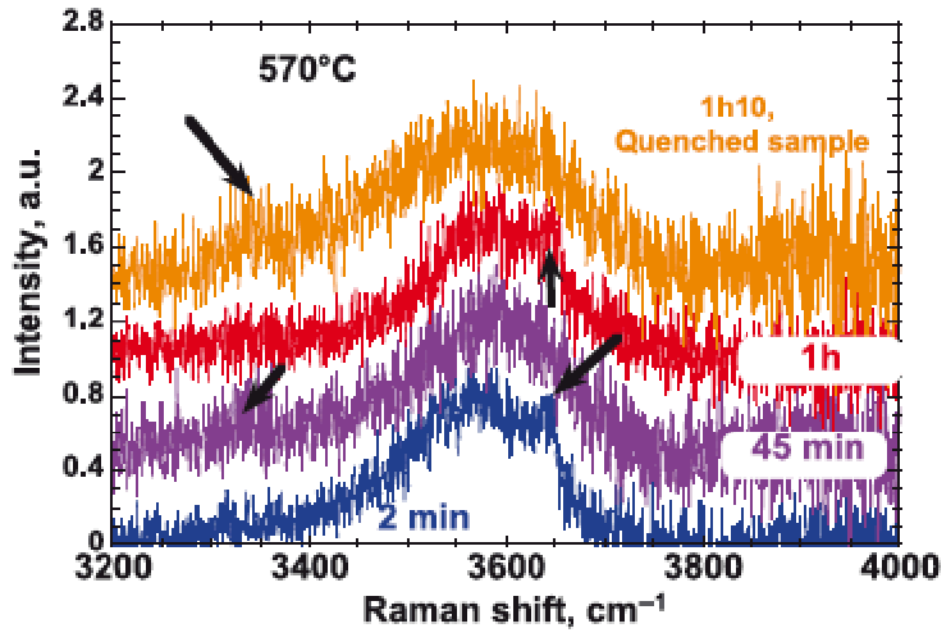
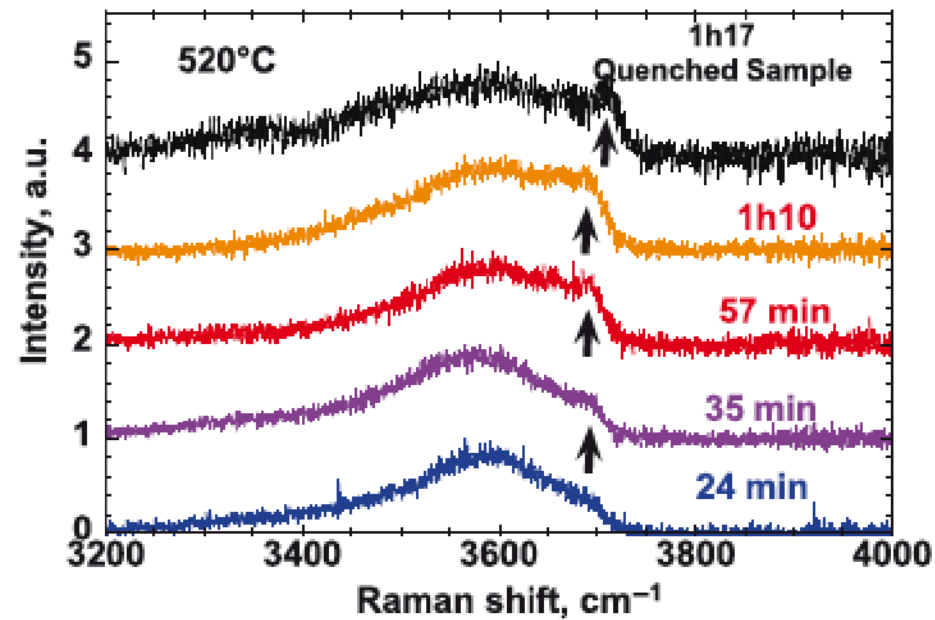


Magnien V., Neuville D.R., Cormier L., Roux J., Pinet O. and Richet P. (2006) Kinetics of iron redox reactions: A high-temperature XANES and Raman spectroscopy study. *Journal of Nuclear Materials*, 352, 190-195.

Speciation and amphoteric behaviour of water in aluminosilicate melts and glasses: high-temperature Raman spectroscopy and reaction equilibria

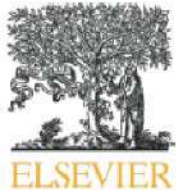
CHARLES LE LOSQ¹, ROBERTO MORETTI^{2,3} and DANIEL R. NEUVILLE^{1,*}





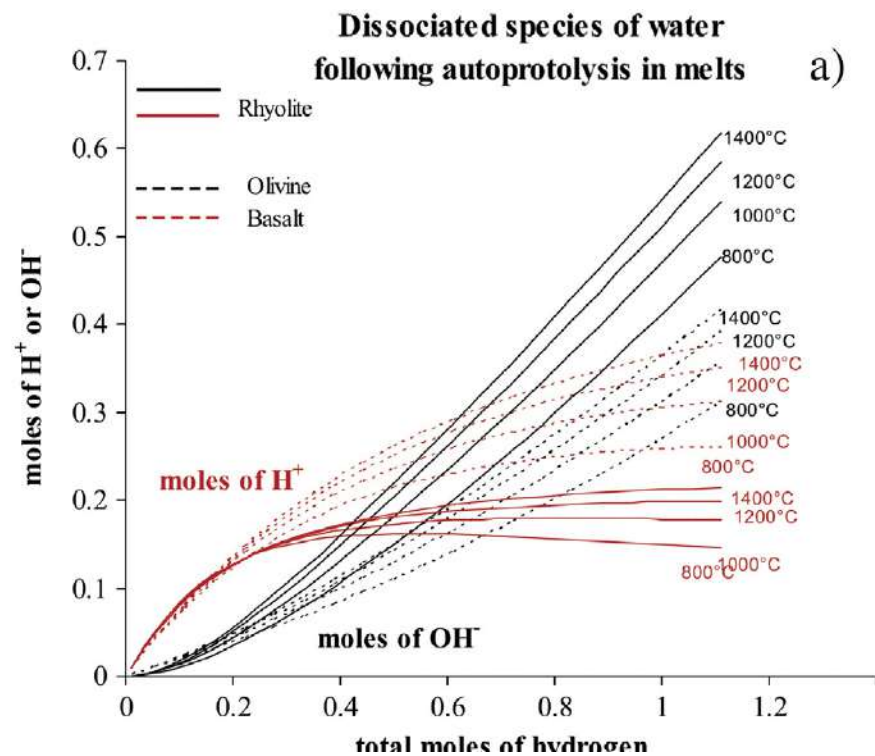
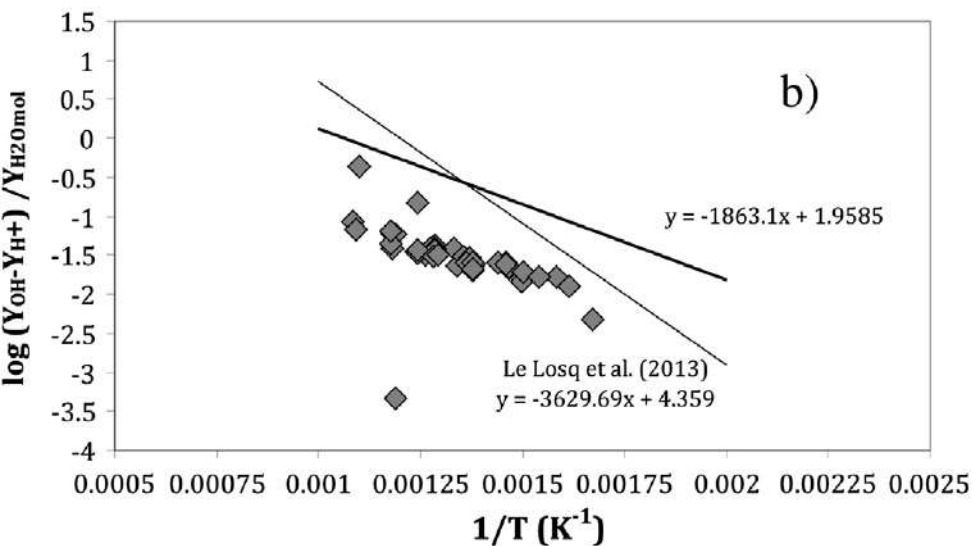
Possibilité de quantifier la teneur en volatils en fonction de X et T

Possibilité de suivre des réactions de déshydration, décarbonatation.....

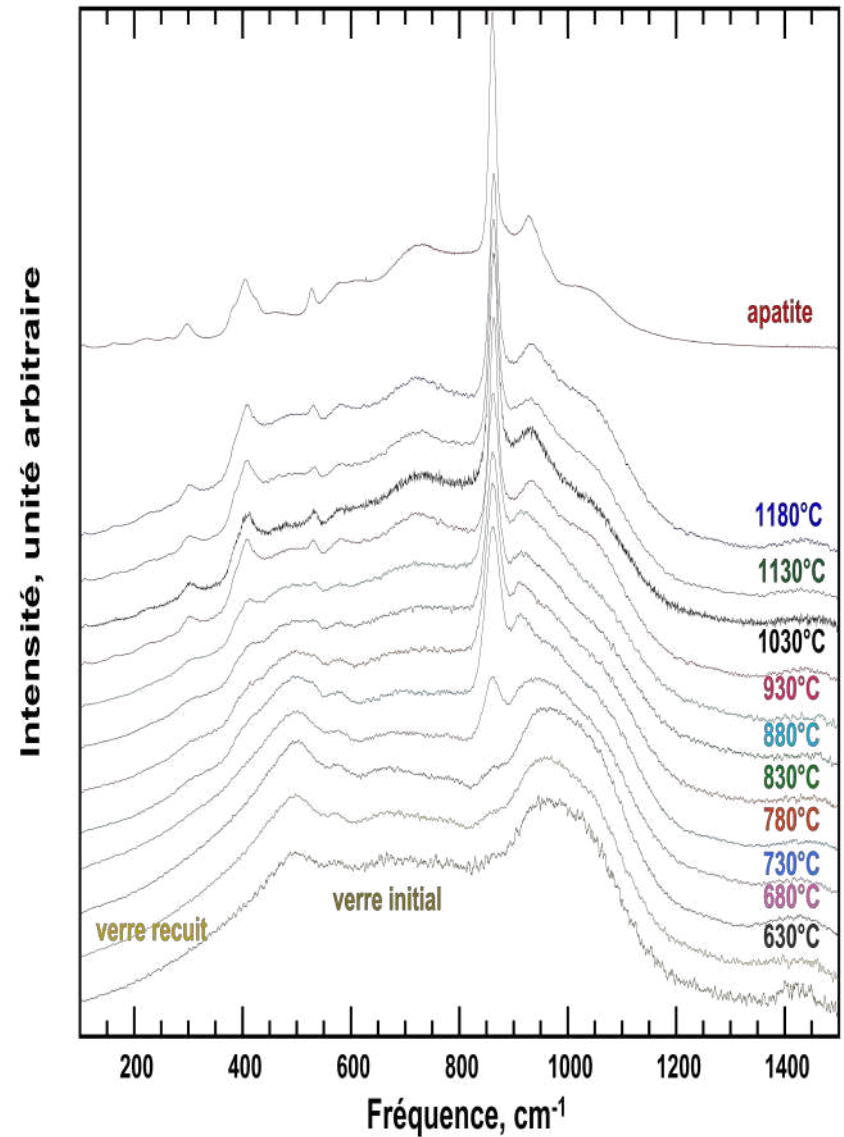
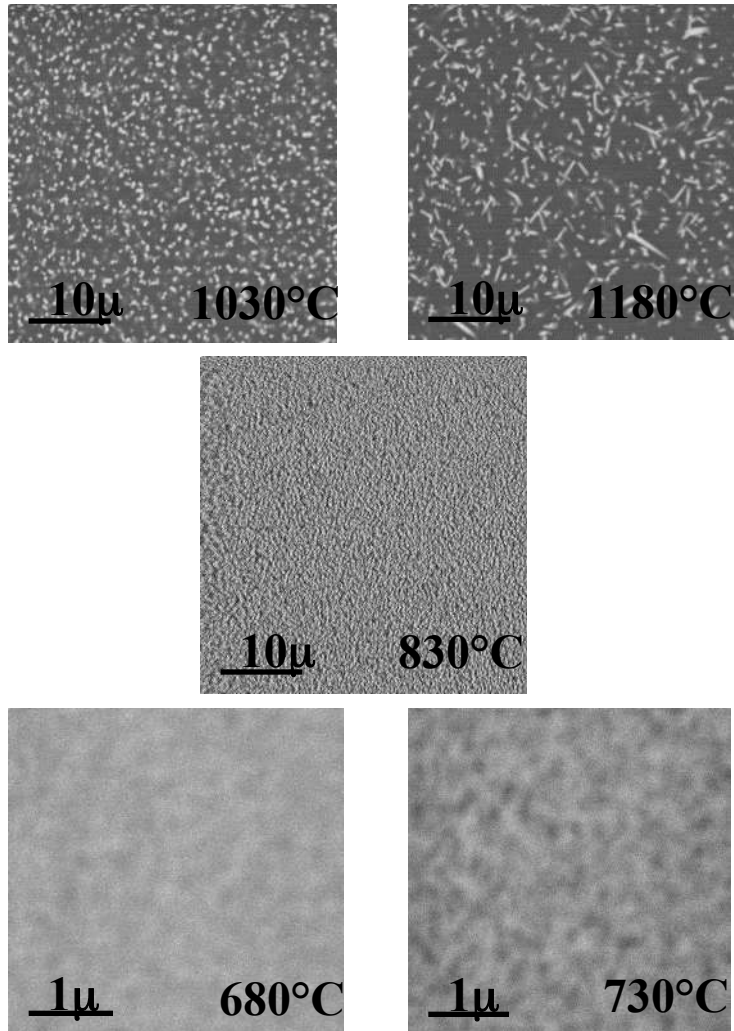


The amphoteric behavior of water in silicate melts from the point of view of their ionic-polymeric constitution

Roberto Moretti^{a,b,c,*}, Charles Le Losq^{d,1}, Daniel R. Neuville^d



Et pour finir, un petit rapport Raman en T, possibilité de suivre cinétique de cristallisation, ...

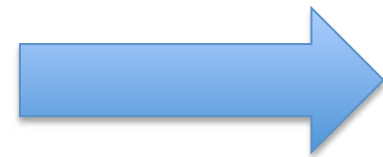


Raman en Température :

- ⇒ Possibilité de caractérisation d'espèce cristallisante
- ⇒ Possibilité de suivre réaction entre espèces, grandeur réactionnelle ΔH
- ⇒ Suivie de cinétique rédox, de réaction de déshydrations....
- ⇒ Facile de mettre en œuvre,

seul facteur limitant l'imagination !

⇒ Et pour en savoir plus





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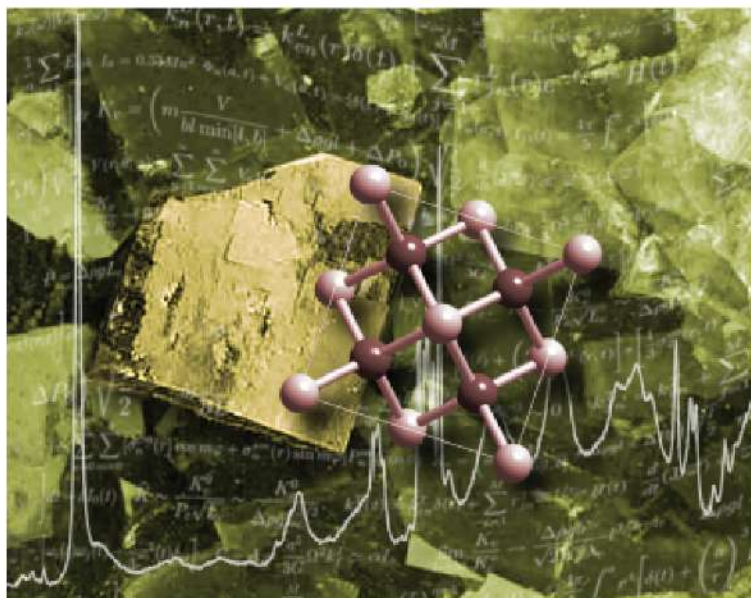
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SPECTROSCOPIC METHODS

in Mineralogy and Materials Sciences

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Daniel R. Neuville, Robert T. Downs



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Advances in Raman Spectroscopy Applied to Earth and Material Sciences

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