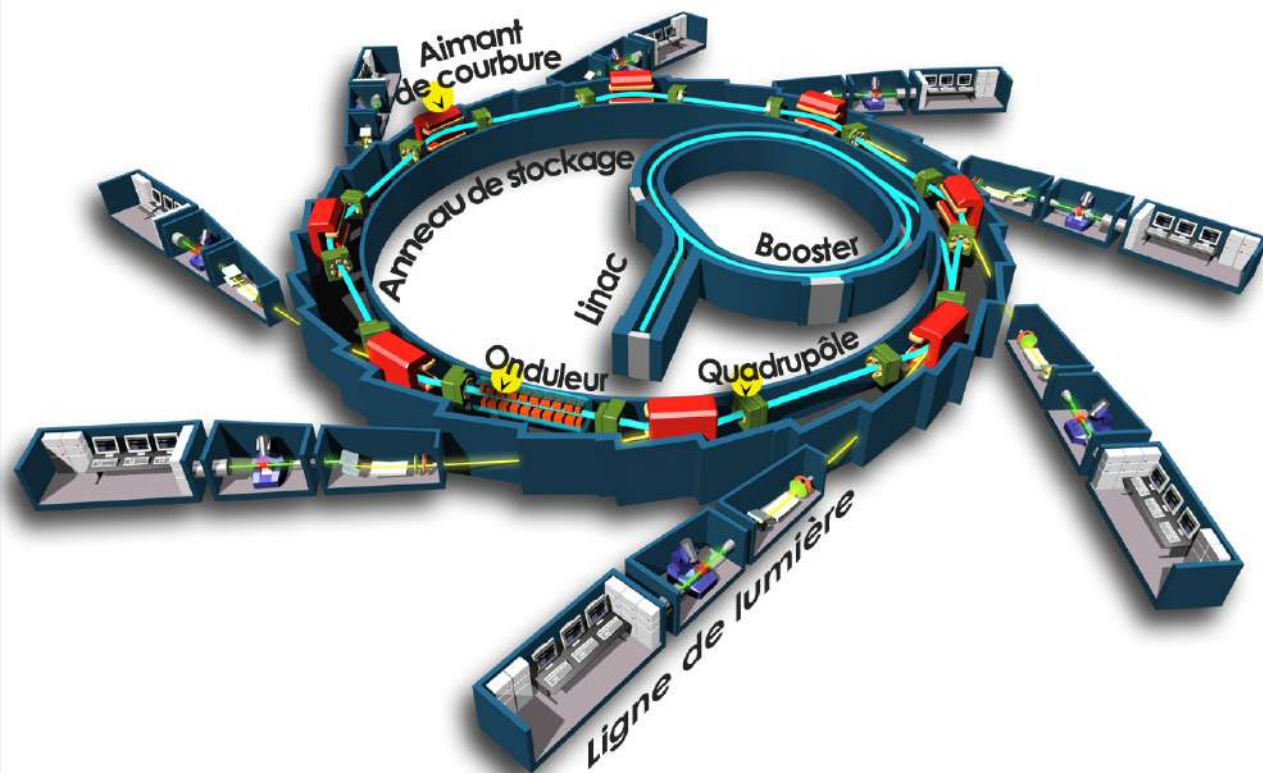


# Grands instruments, vers des approches *in situ* de la cristallisation

Daniel R. Neuville et Laurent Cormier



## Source de Rayon X

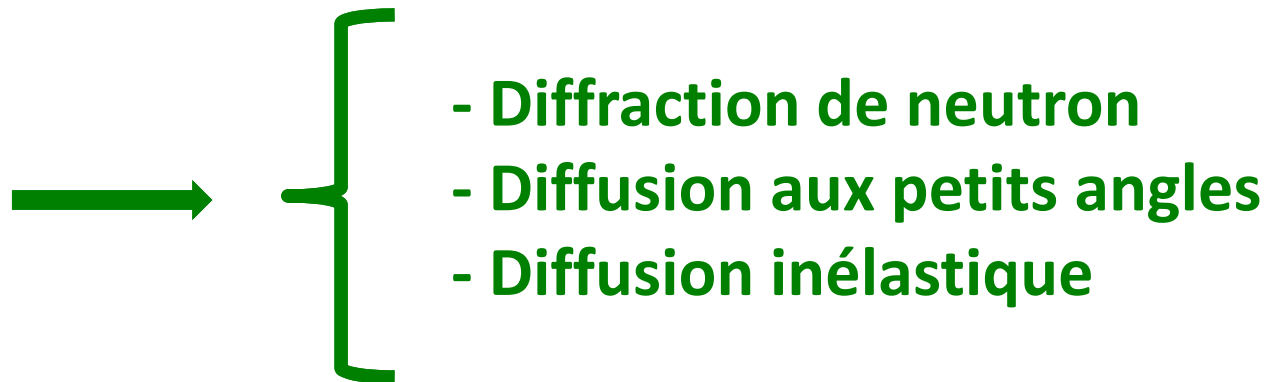
- Focalisé
- Haute énergie
- Résolue en temps

- 
- Diffraction de rayon X
  - Absorption de rayon X
  - Diffusion aux petits angles
  - Diffusion inélastique
  - Infrarouge

# Les neutrons

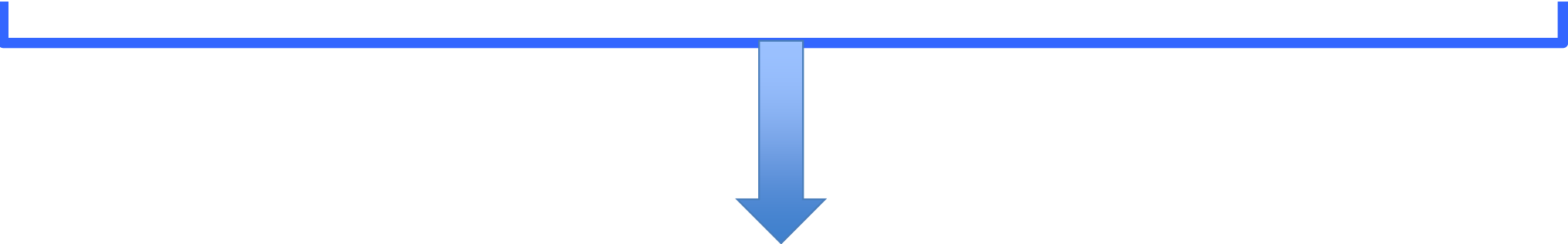
- grand pouvoir de pénétration, non-destructive
- sensibilité au champ magnétique
- sensibilité aux atomes légers, comme l'hydrogène

Source de neutron, les neutrons inter-agissent avec les noyaux de matière. En observant comment ils sont déviés et comment leur vitesse est modifiée, on identifie très précisément la position des atomes et leurs mouvement



Étude classique en utilisant la diffraction de rayon X de neutron, les spectroscopie Raman, IR, absorption de rayon X, RMN...

Mécanismes de nucléation et croissance bien connus dans  $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ ,  $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ ,  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  :



**expériences *in situ* sont difficiles mais donnent des informations en temps réel, sur la structure et les mécanismes de nucléation**

# Cellule Linkam®



- Ambiante à 1500°C
- Atmosphère contrôlé
- Volume échantillon ~mm

=> Analyse en réflexion

# DUBBLE-ESRF

Faisceau incident

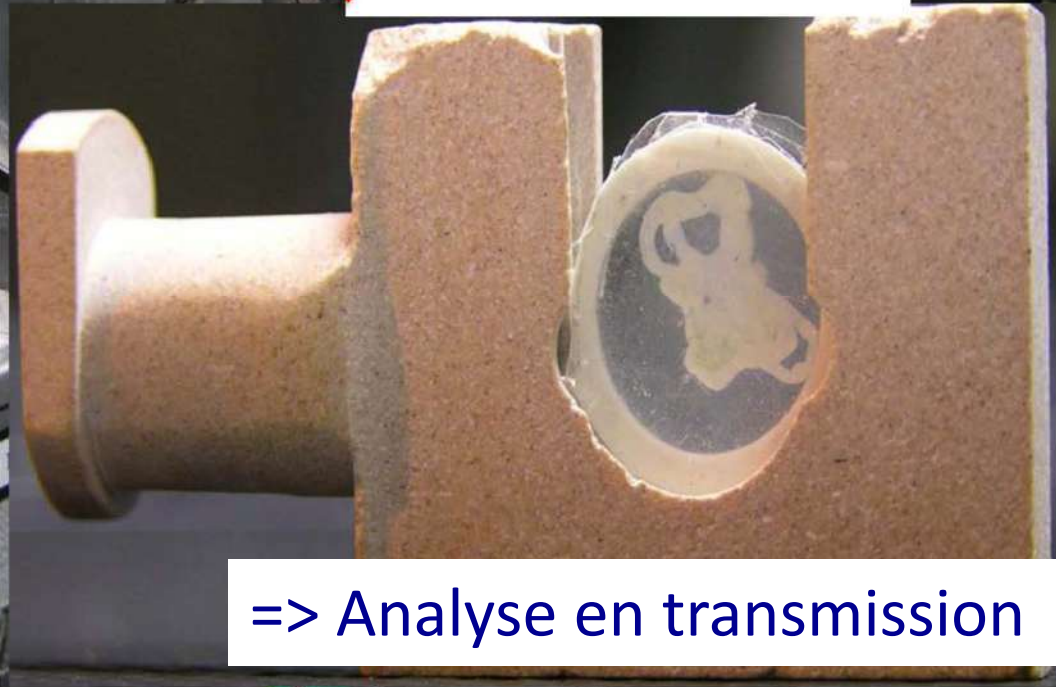
Vers détecteur de fluorescence XAS

Échantillon, 1cm

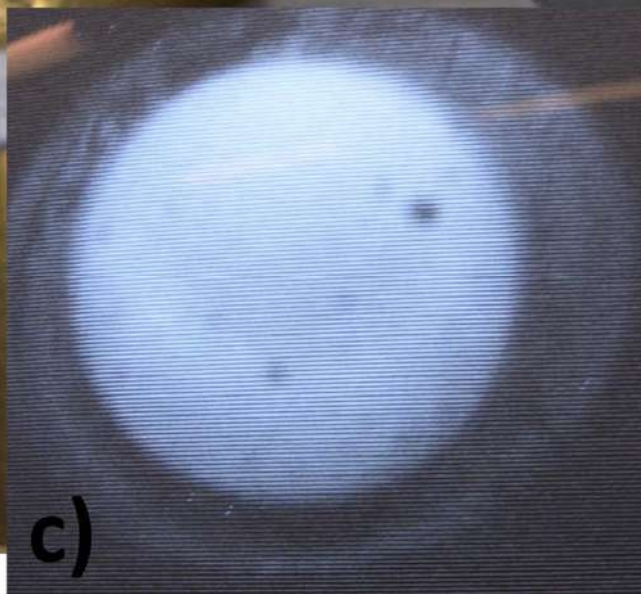
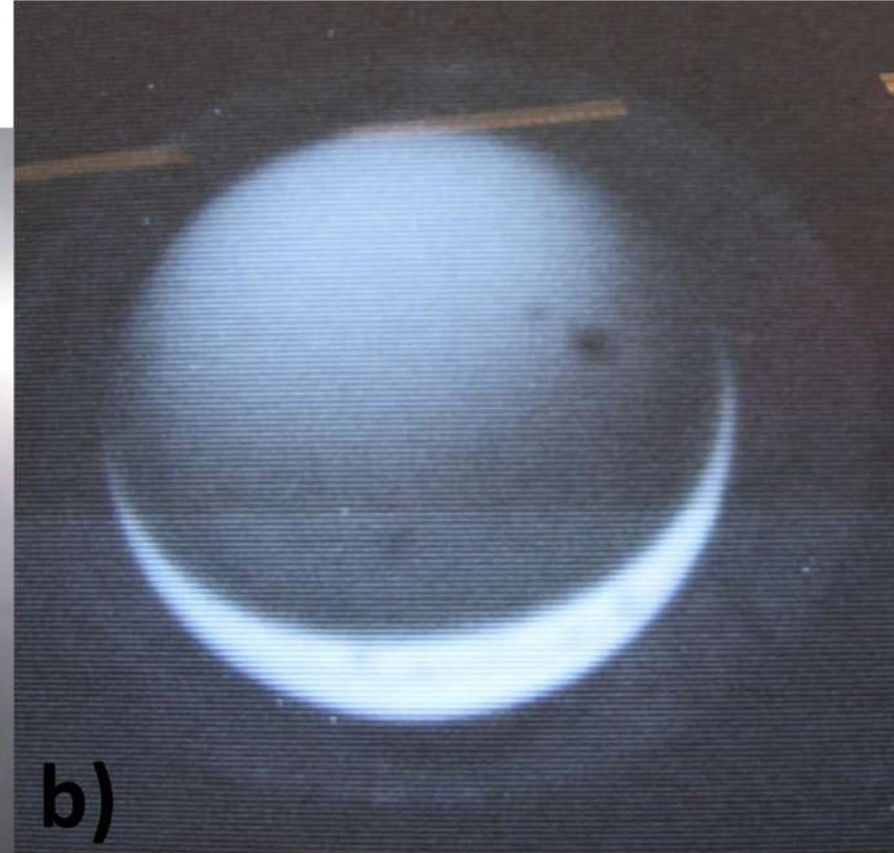
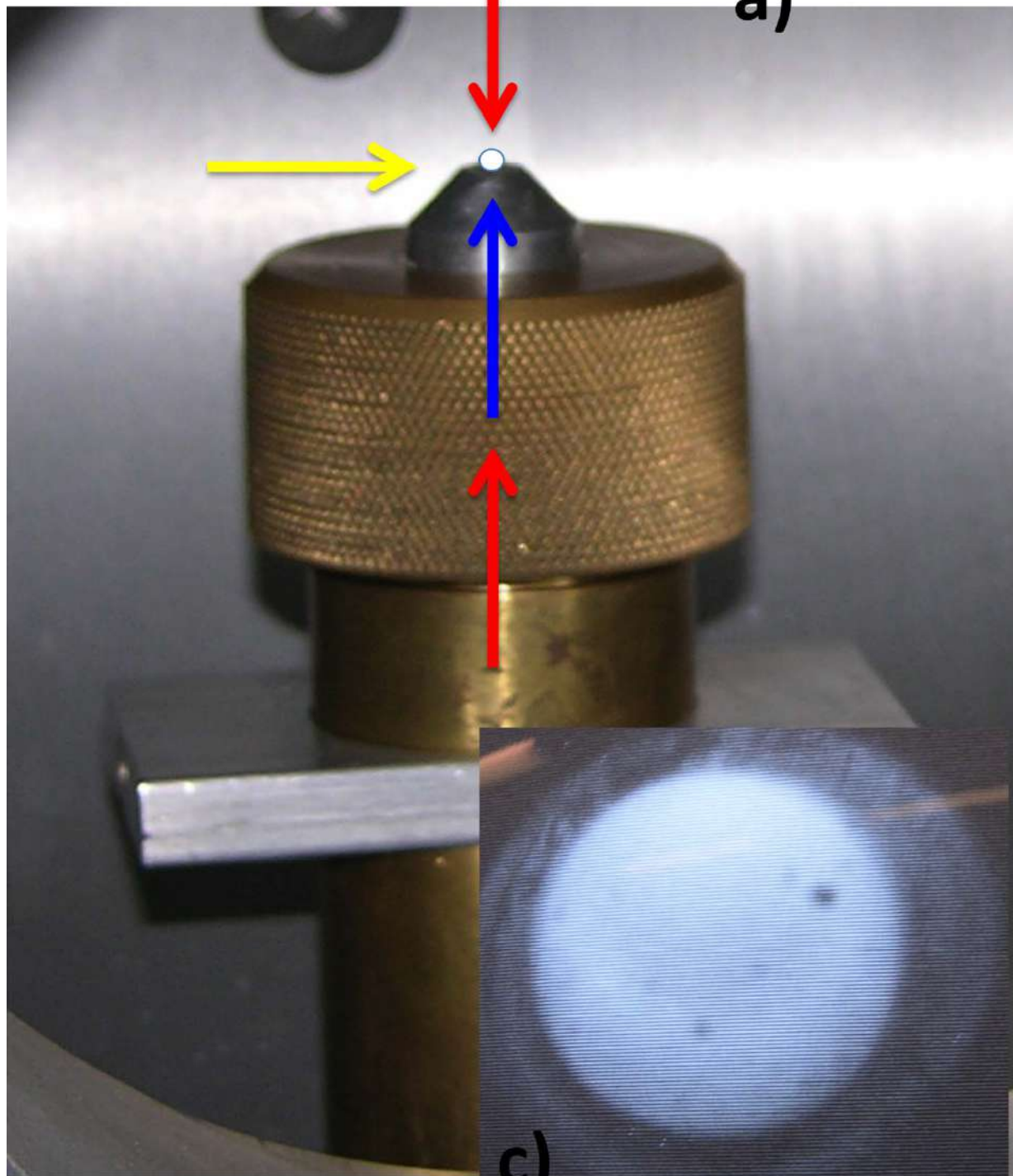
WASX et XAFS transmis

- Ambiante à 1000°C
- Atmosphère contrôlé
- échantillon ~1cm\*1mm

=> Analyse en transmission

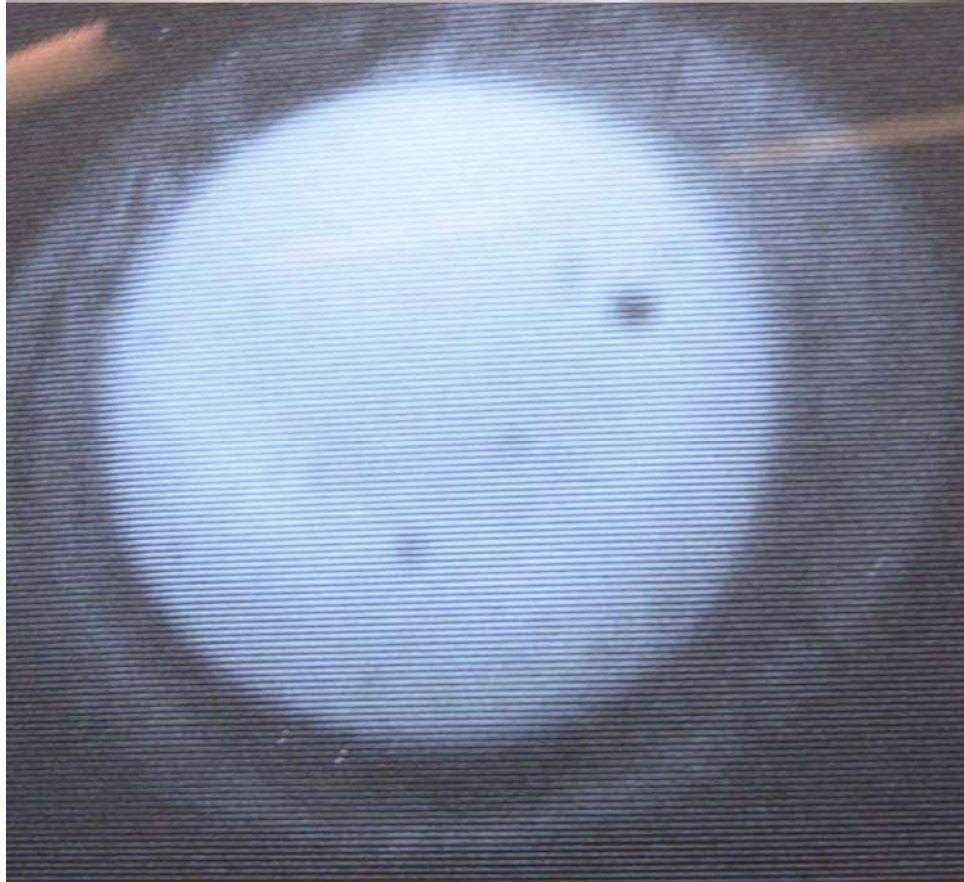


Chauffage en lévitation





Buse : Cu, Dural, Vanadium....

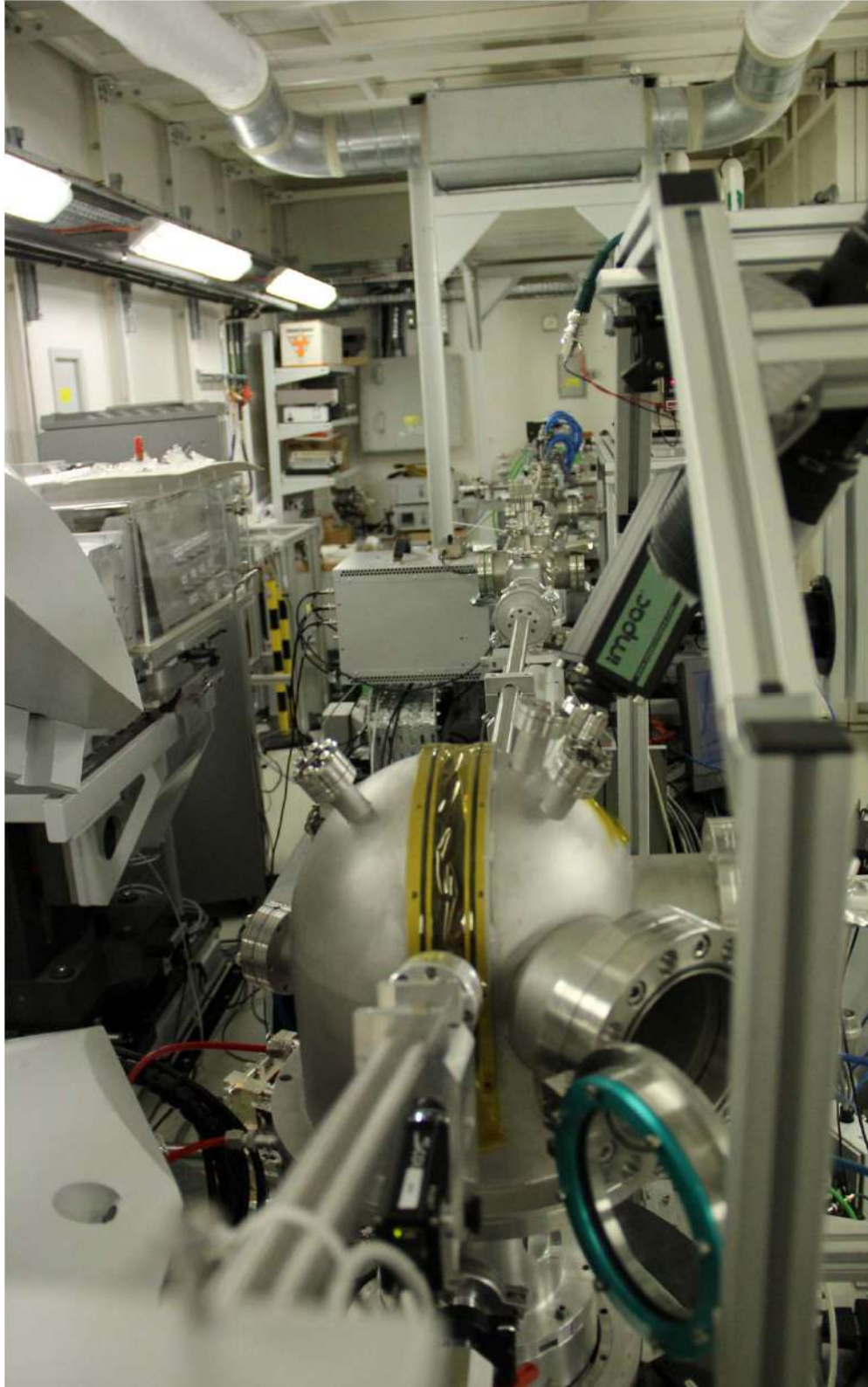


- Ambiante à 3000°C
- Atmosphère contrôlé
- Échantillon sphère ~1mm

**=> Analyse en transmission  
et en surface**

Merci à L. Hennet, CEMHTI-CNRS

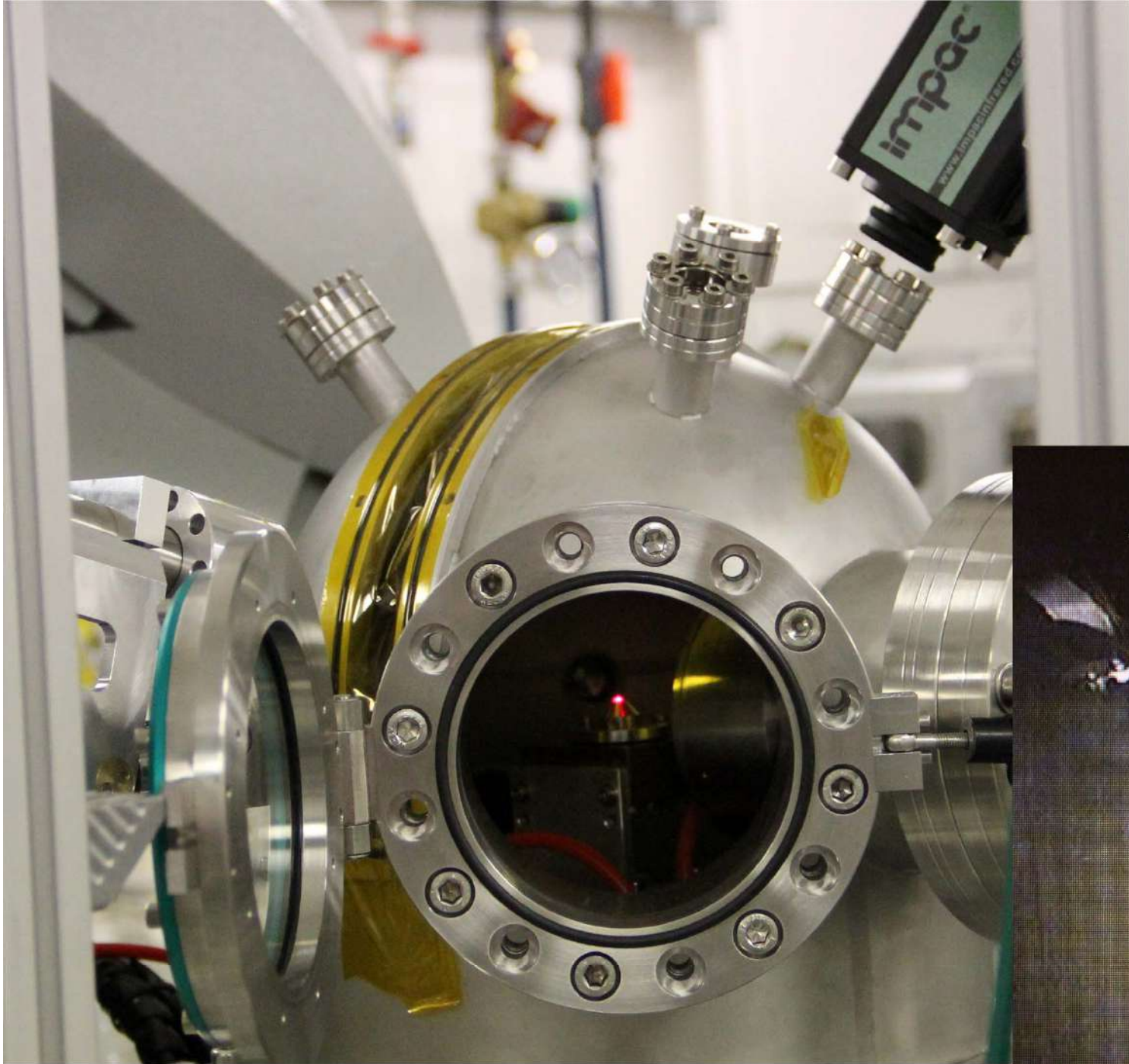


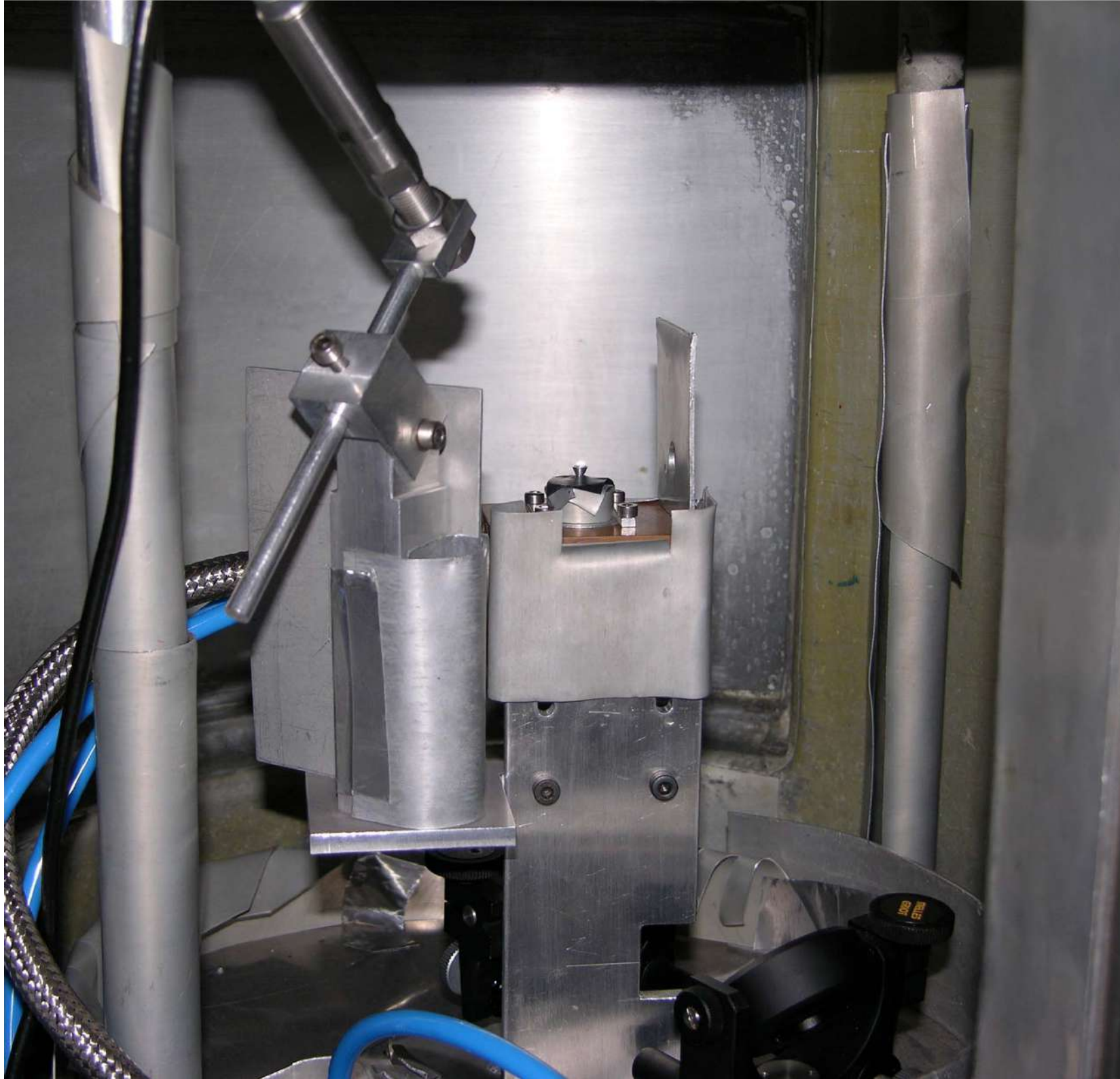


# DIFFABS-SOLEIL

Merci à  
Dominique Thiaudière (SOLEIL)  
Louis Hennet (CEMHTI-CNRS)

# DIFFABS-SOLEIL





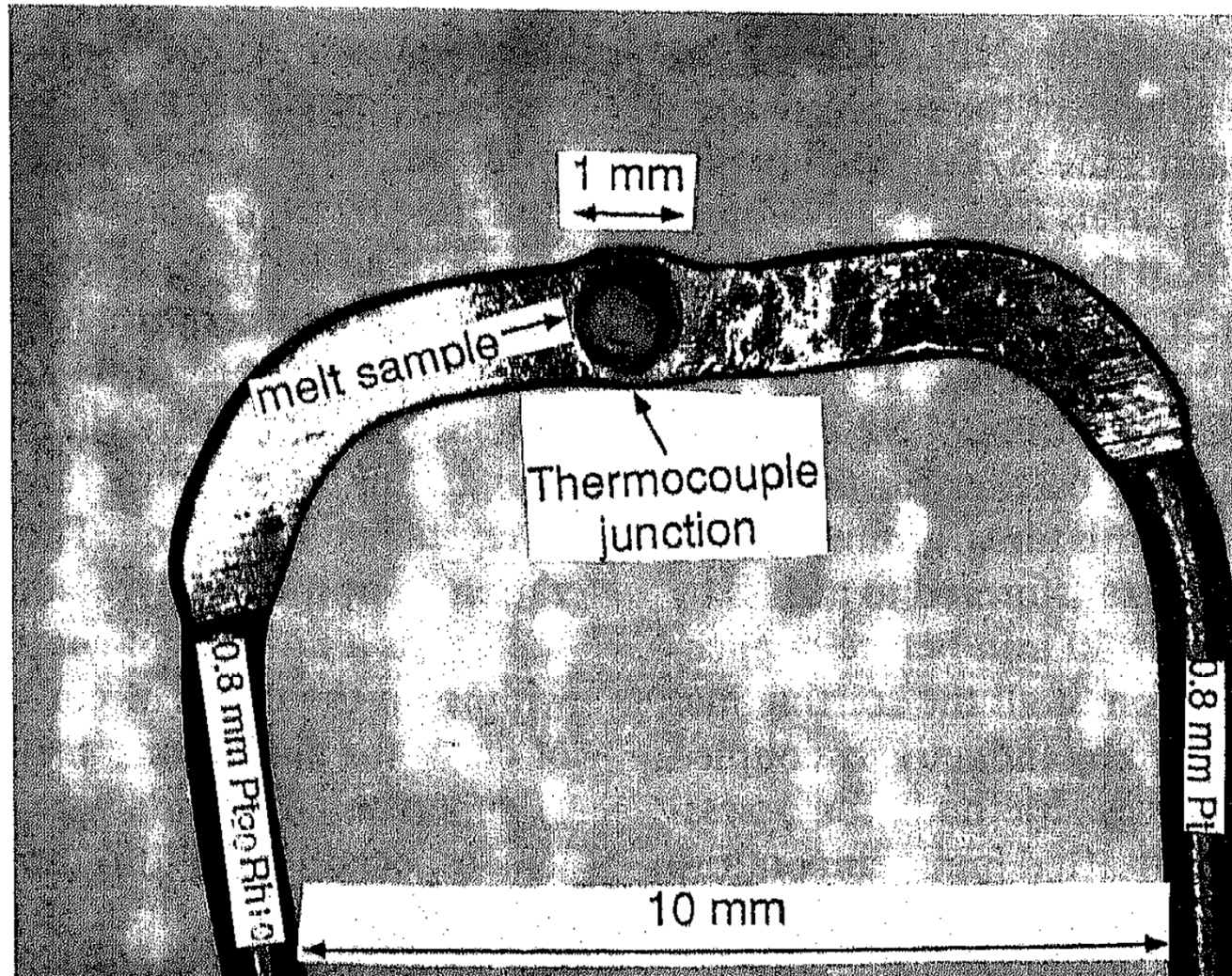
D6-ILL

Merci à  
Henri Fisher (ILL)  
Louis Hennet  
(CEMHTI-CNRS)

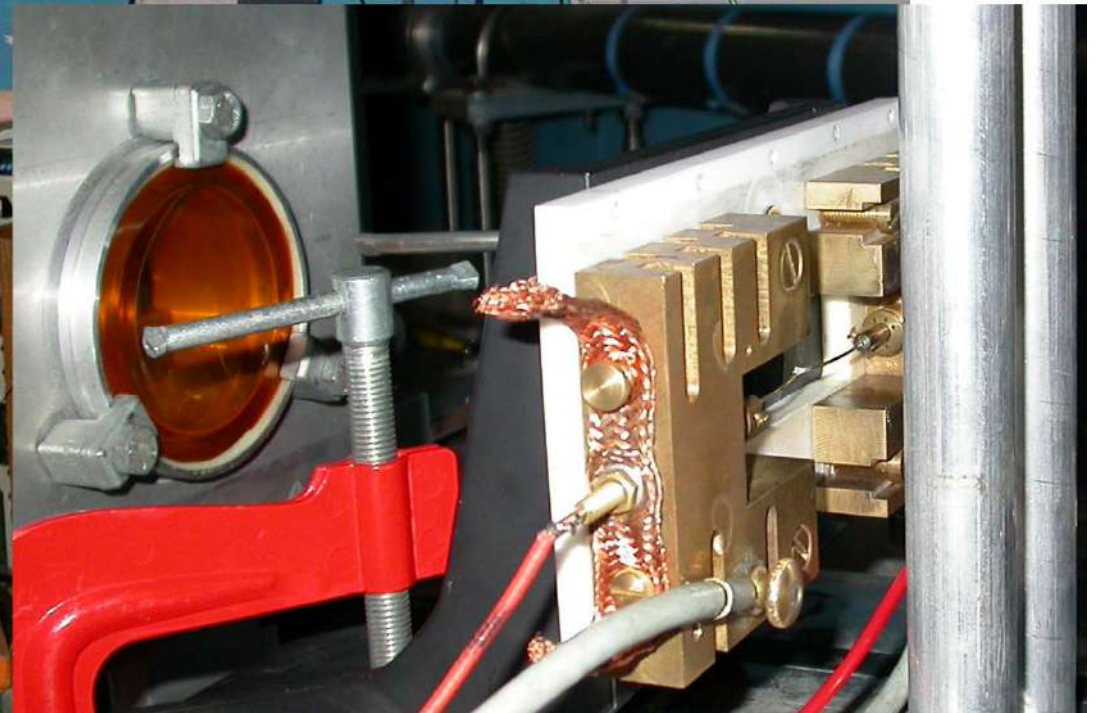
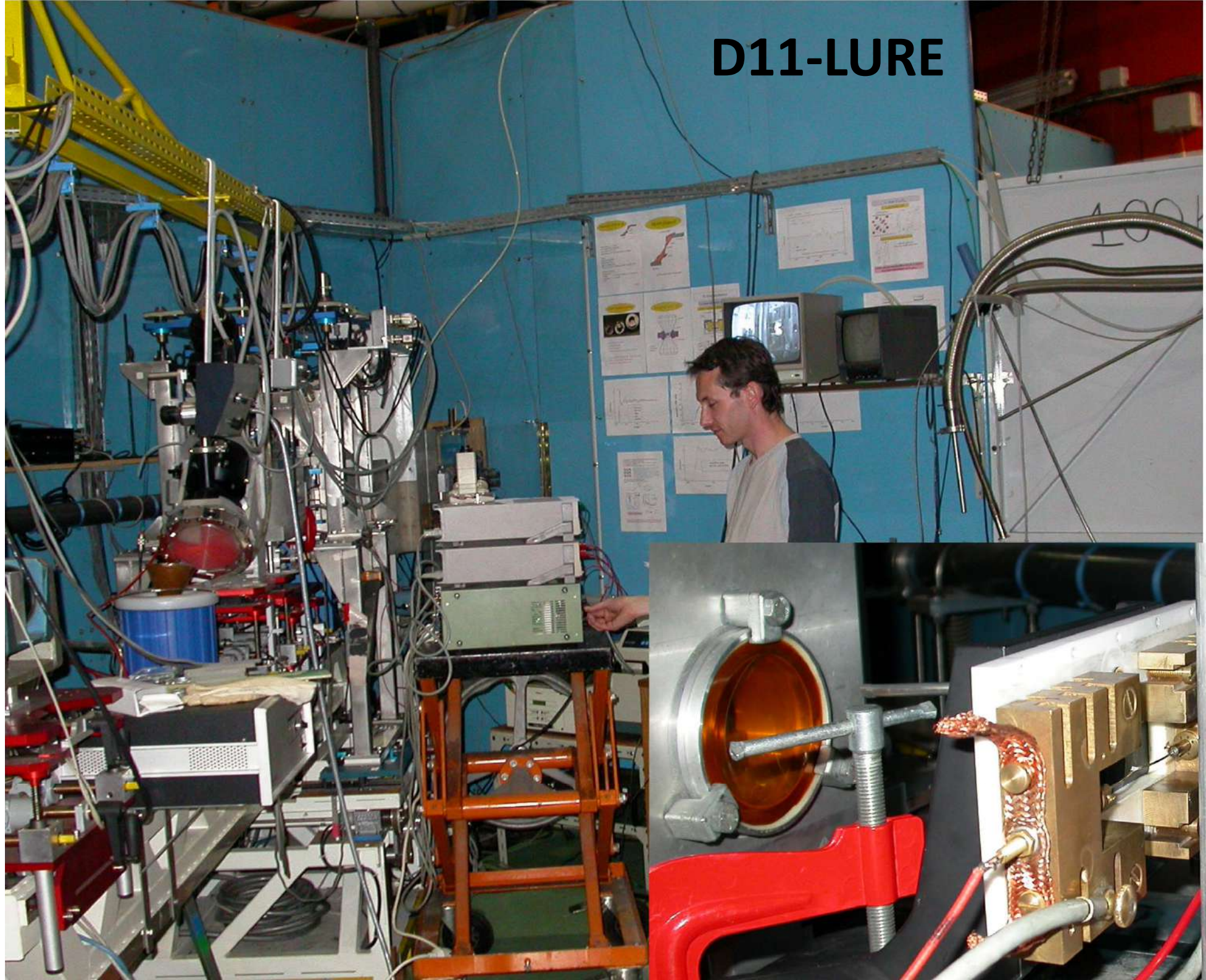
# Raman spectroscopy of silicate melts at magmatic temperatures: $\text{Na}_2\text{O}-\text{SiO}_2$ , $\text{K}_2\text{O}-\text{SiO}_2$ and $\text{Li}_2\text{O}-\text{SiO}_2$ binary compositions in the temperature range 25–1475°C

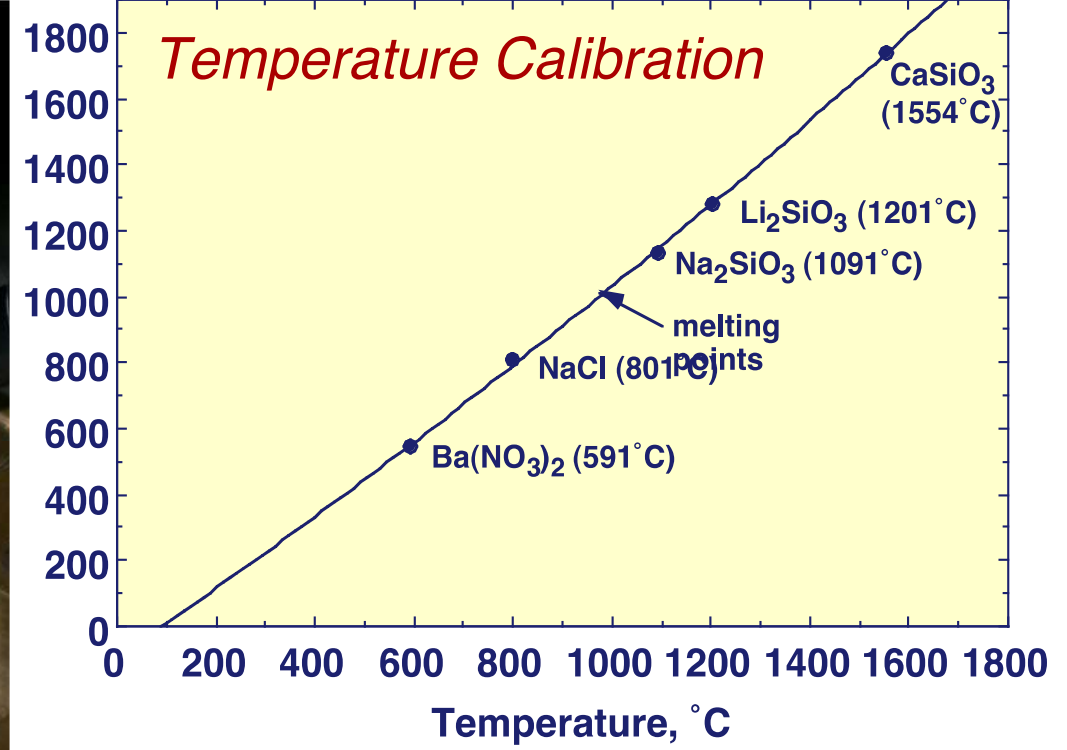
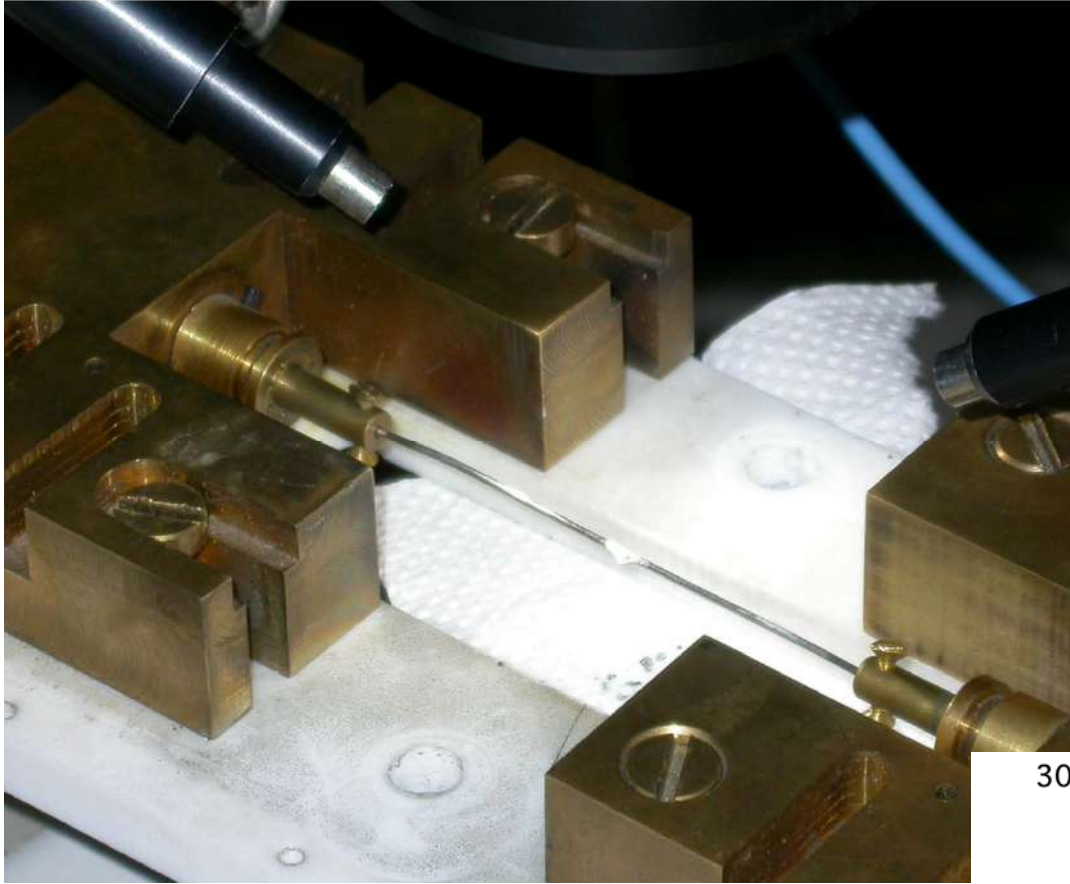
Bjorn O. Mysen and John D. Frantz

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

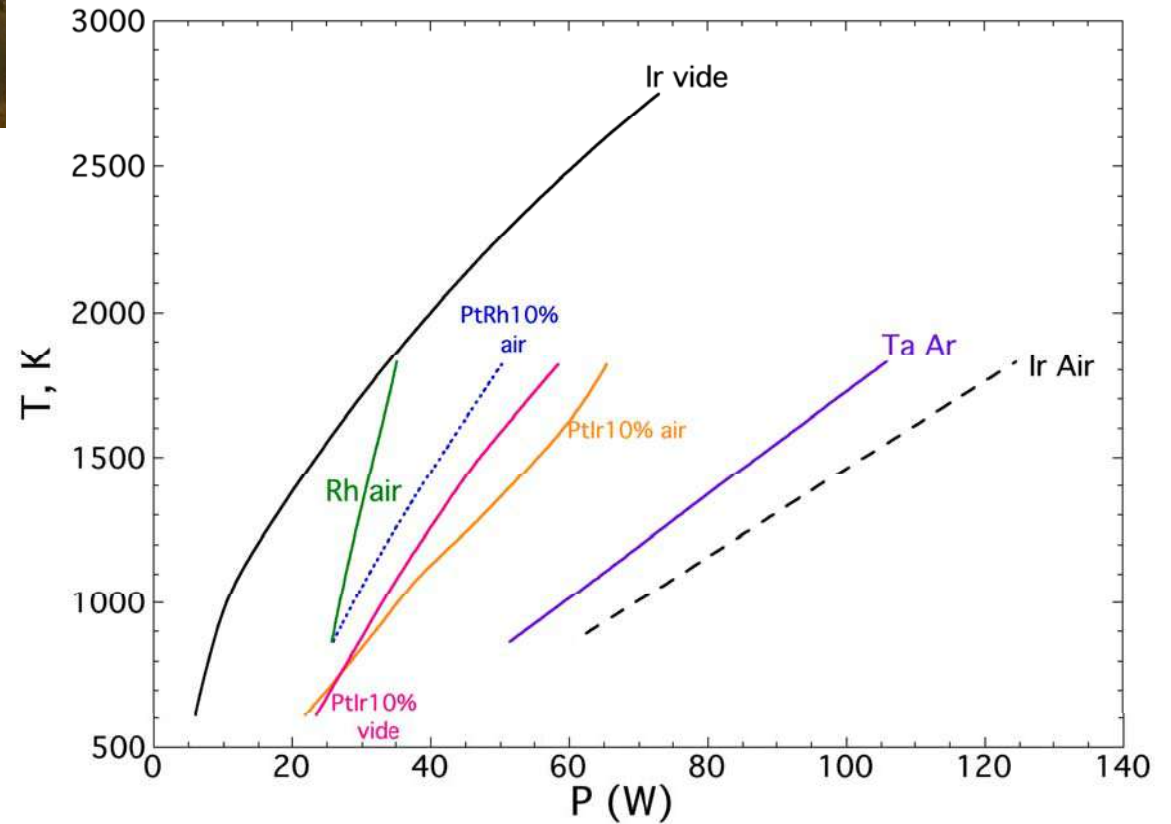


# D11-LURE





Fil : Pt, Pt/Rh, Pt/Ir, W, Rh, Ta  
Différente fO<sub>2</sub>



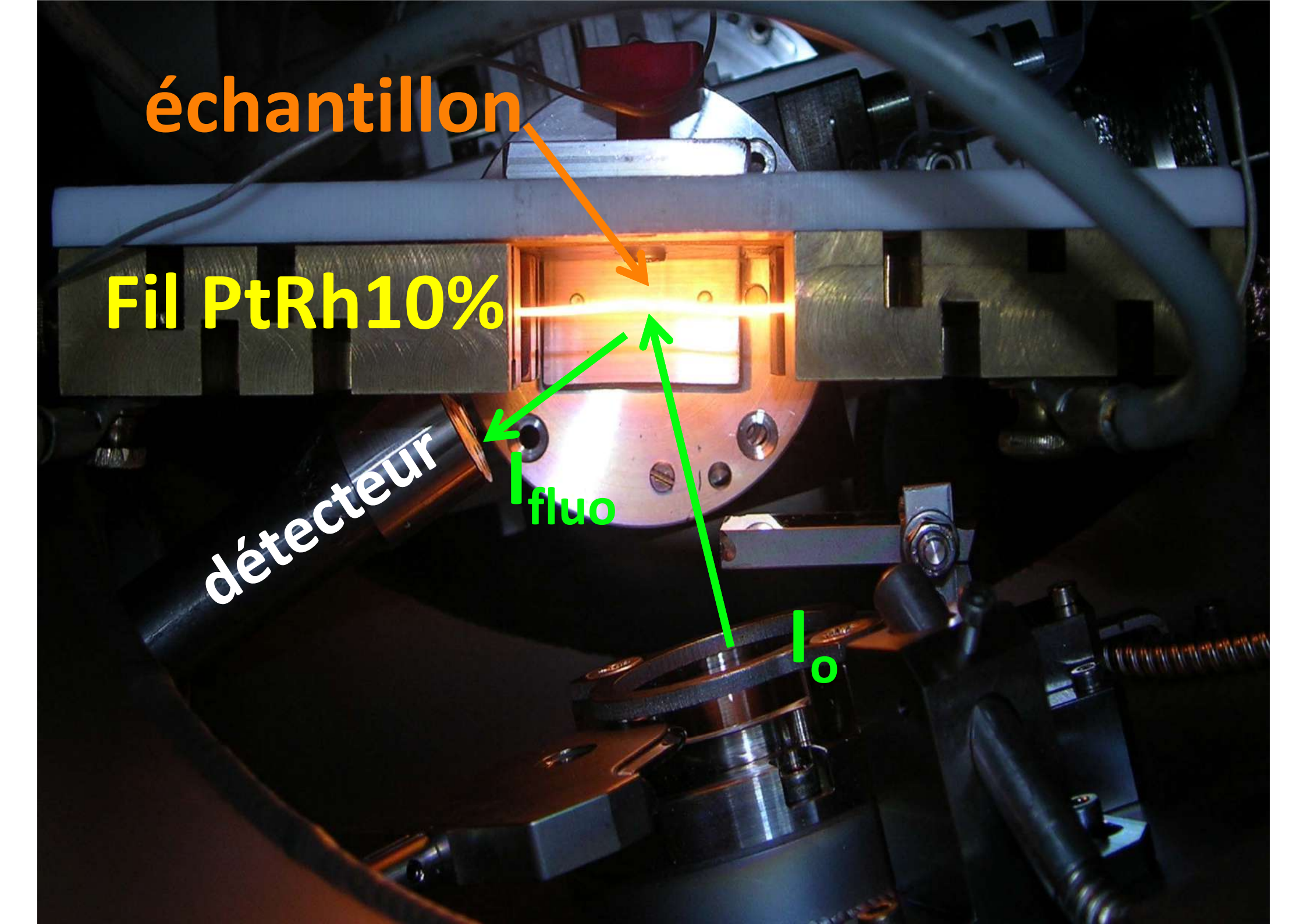
échantillon

Fil PtRh10%

détecteur

I<sub>fluo</sub>

I<sub>o</sub>



**Bulle**

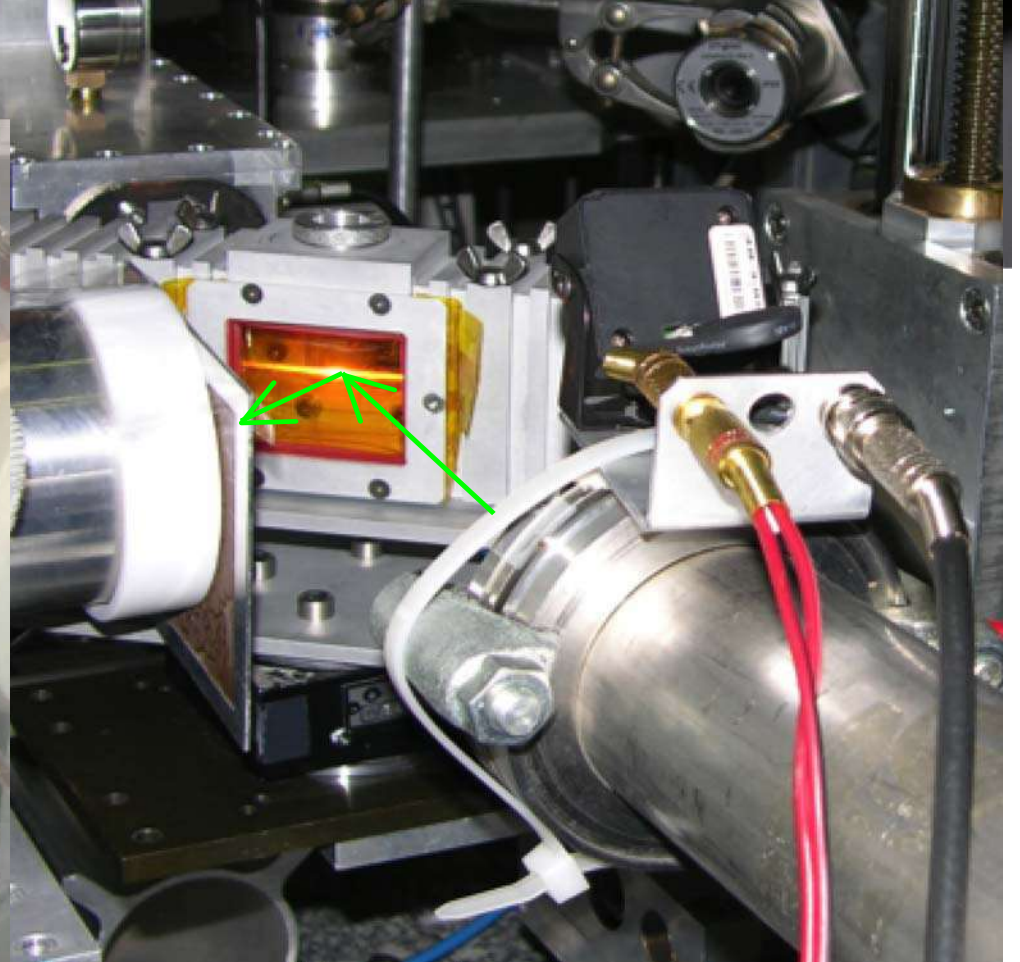
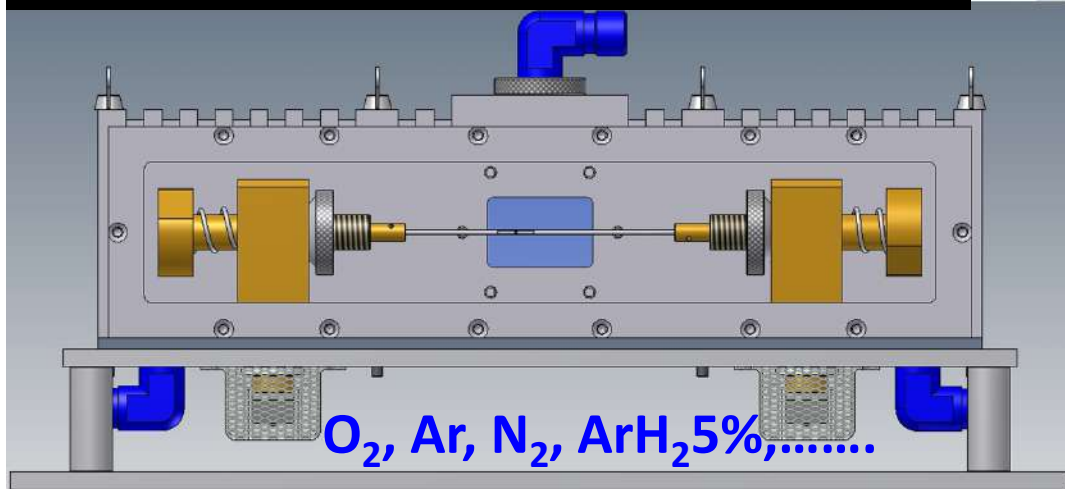
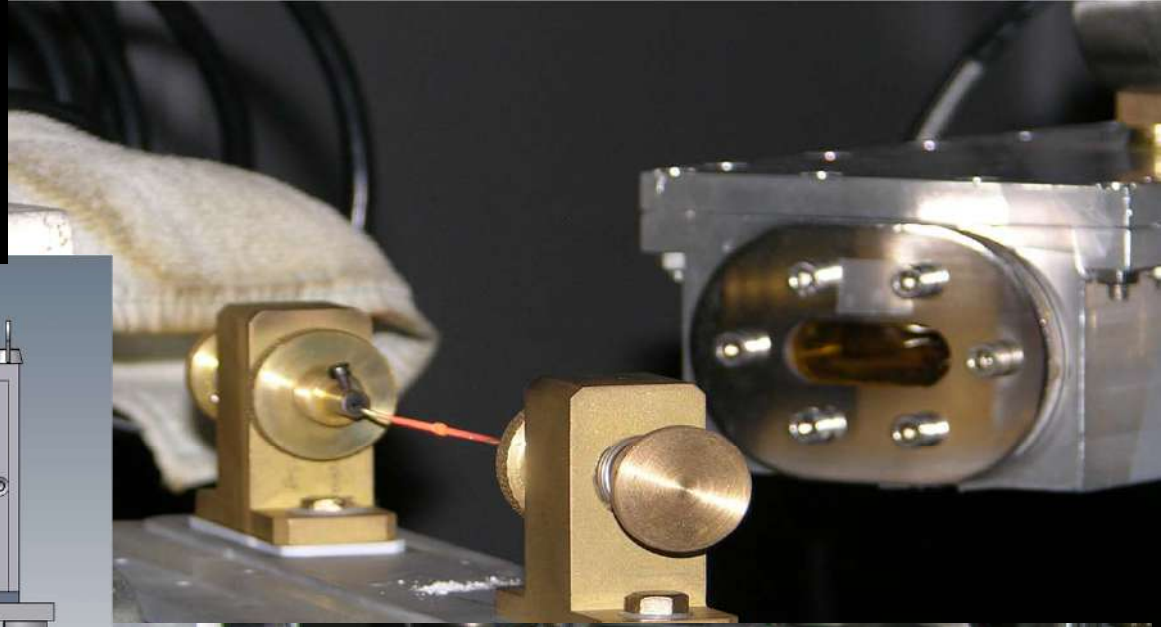


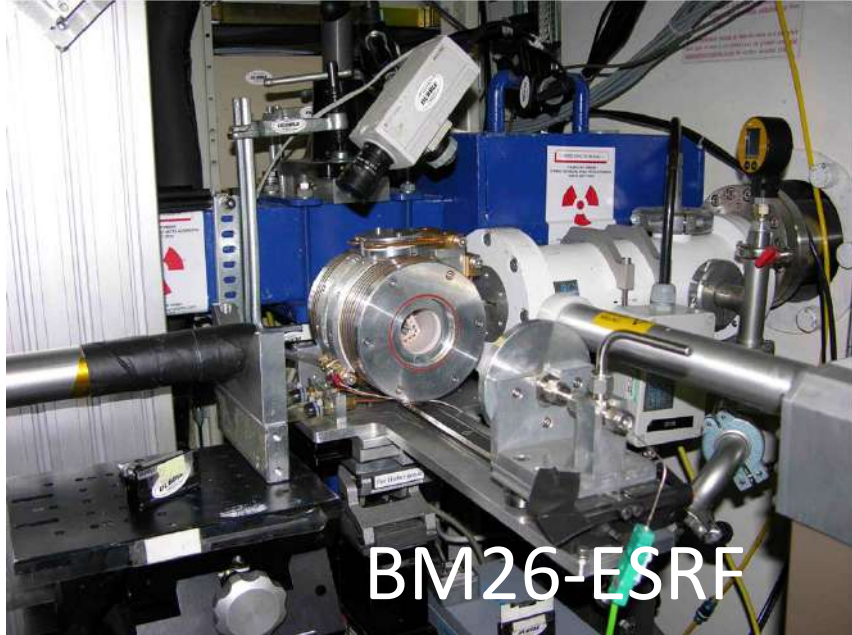
**1<sup>er</sup> cristal**





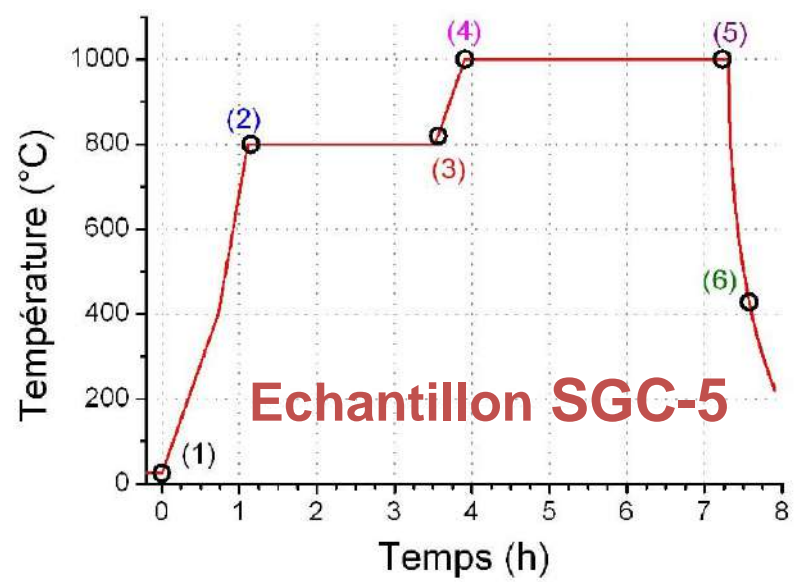
Nouveau système développé entre IPGP-  
CNRS-SGR-Lyon1 et déjà utilisé à XAFS1-  
LNLS, DUBBLE-ESRF, MARS, ODE-SOLEIL  
P. Gonçalves Ferreira, D. de Ligny



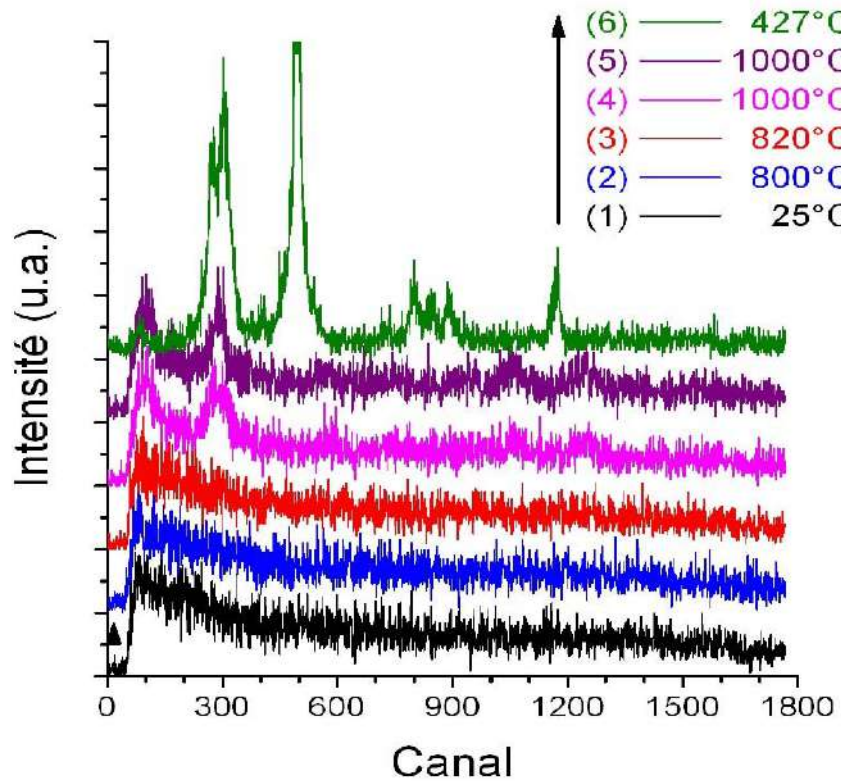


BM26-ESRF

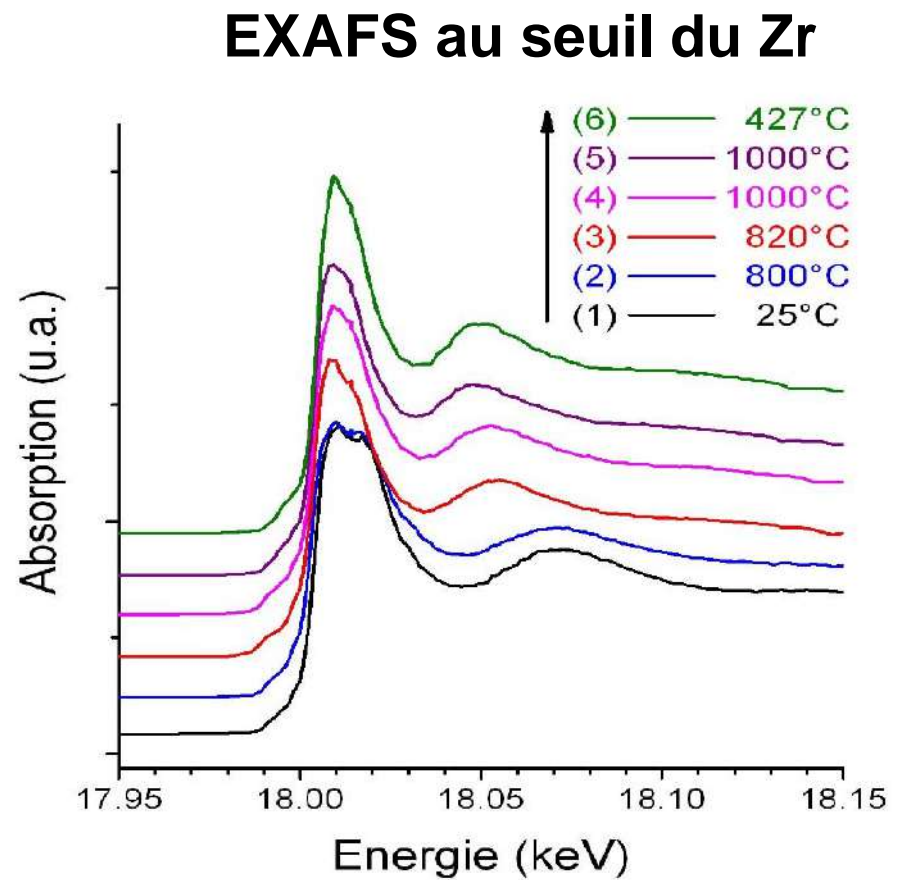
B. Giovanni,  
L. Hennet,  
M. Comte,  
CEMHTI, Corning



### Diffraction

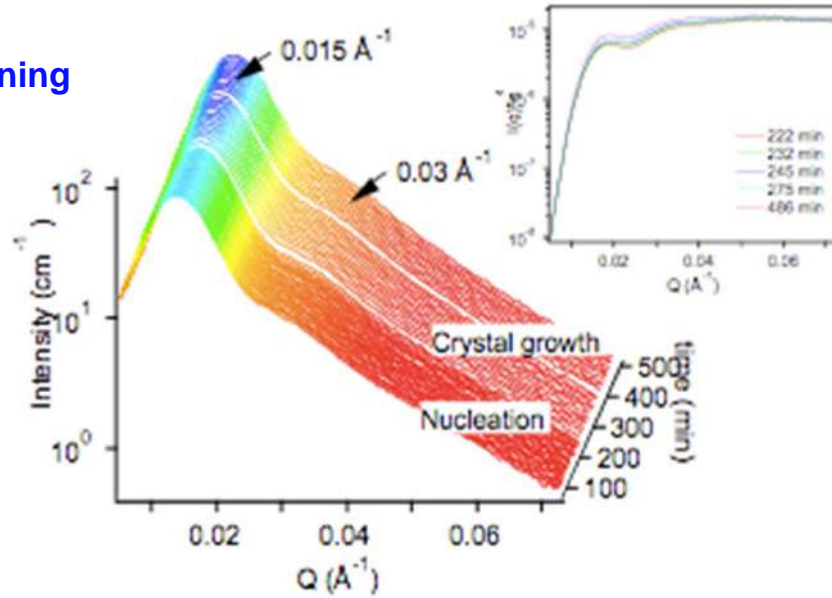


### SAXS

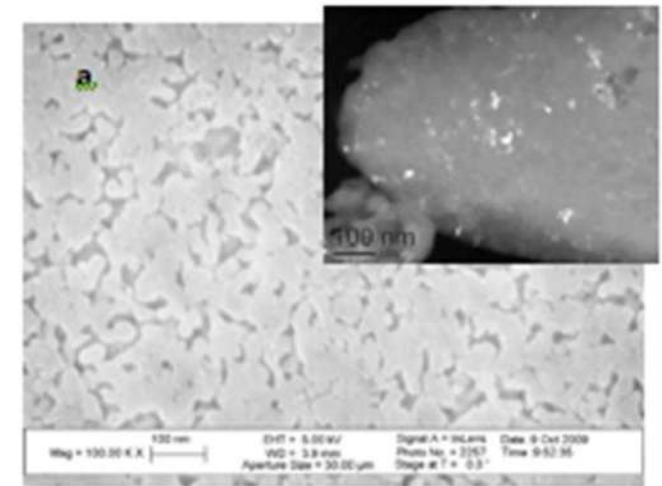




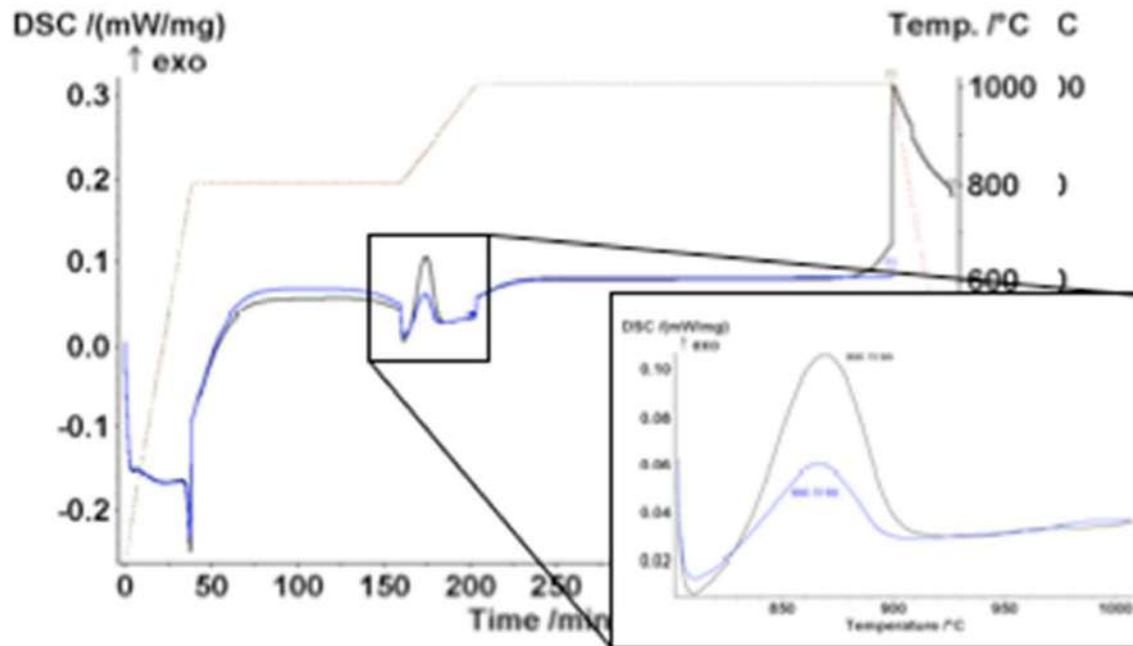
B. Giovanni,  
L. Hennet,  
M. Comte,  
CEMHTI, Corning



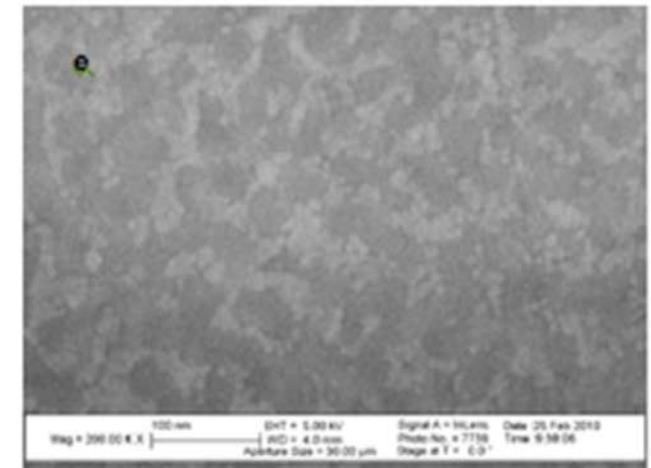
*in-situ* Small Angle Neutron Scattering (SANS),



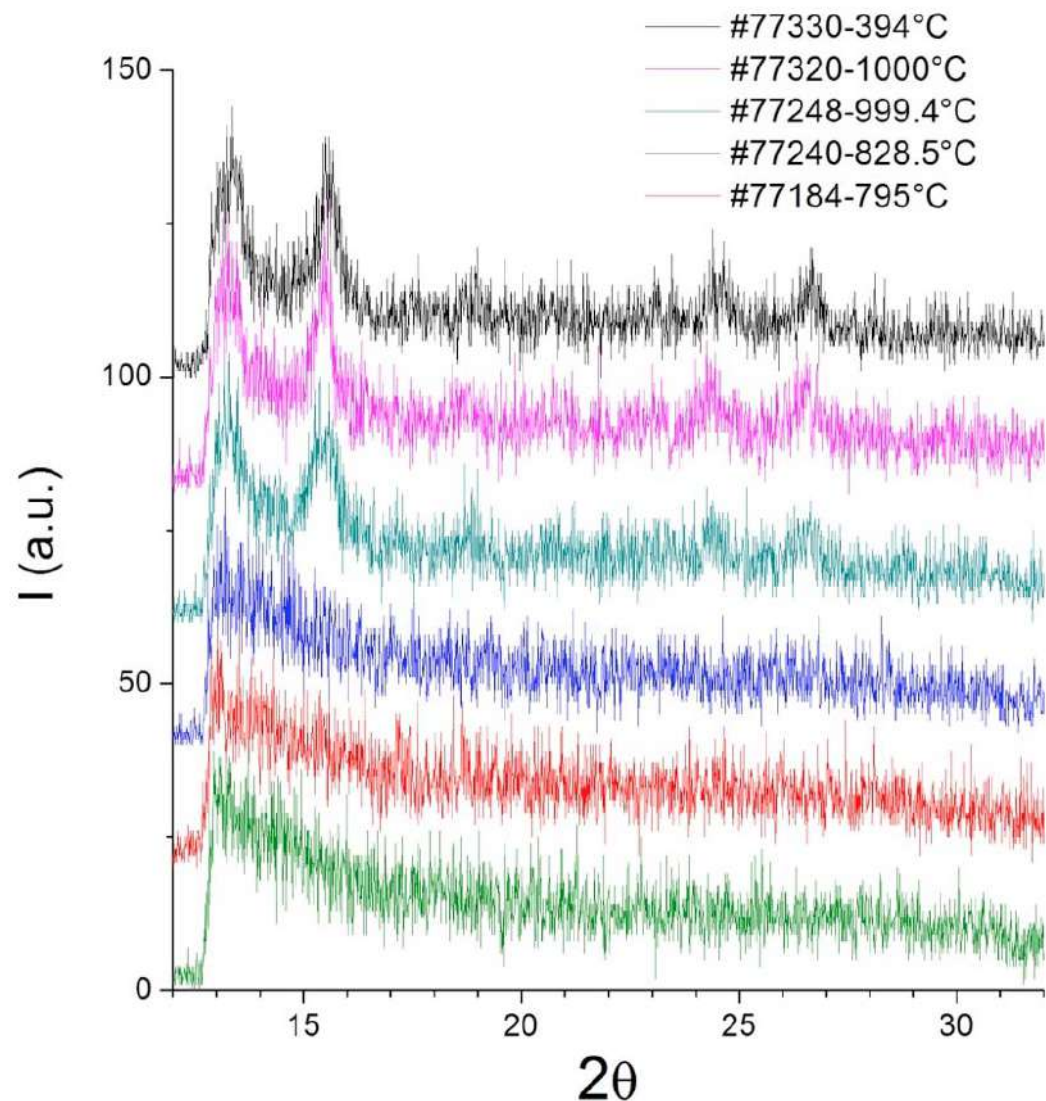
Chauffé jusqu'à fin de  
nucléation



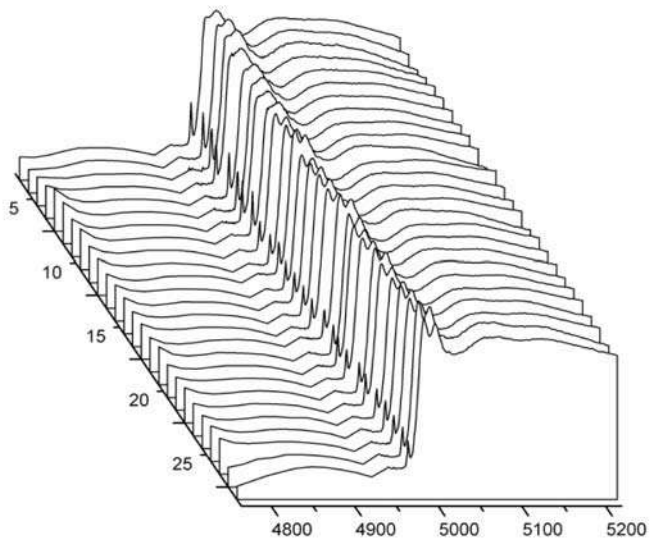
Chauffé jusqu'à fin de  
cristallisation



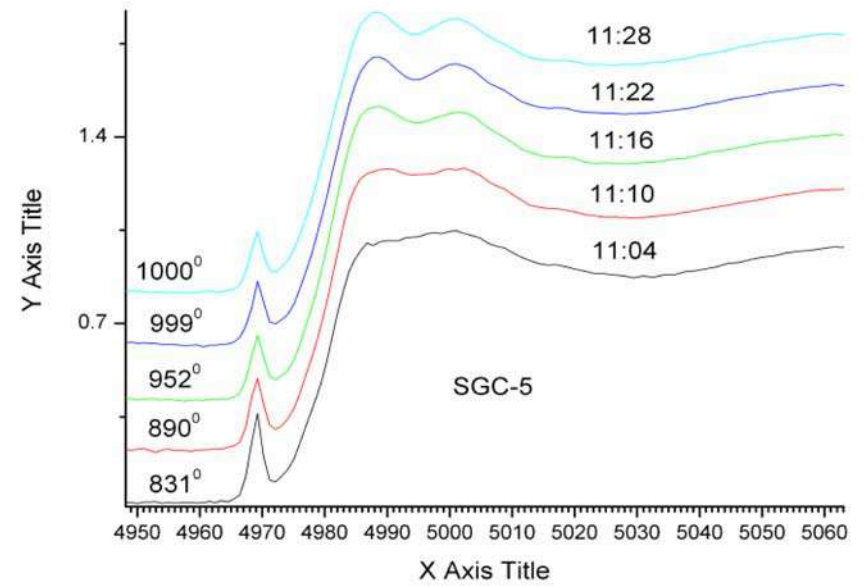
Component (%mol)	LAS	(M,Z)AS	
		SGC72	SGC73
SiO <sub>2</sub>	68	59	59
Al <sub>2</sub> O <sub>3</sub>	19	19	19
Li <sub>2</sub> O	3.5	-	-
MgO+ZnO	3	12	13
TiO <sub>2</sub> +ZrO <sub>2</sub>	4.5	8	8
Others	2	2	1



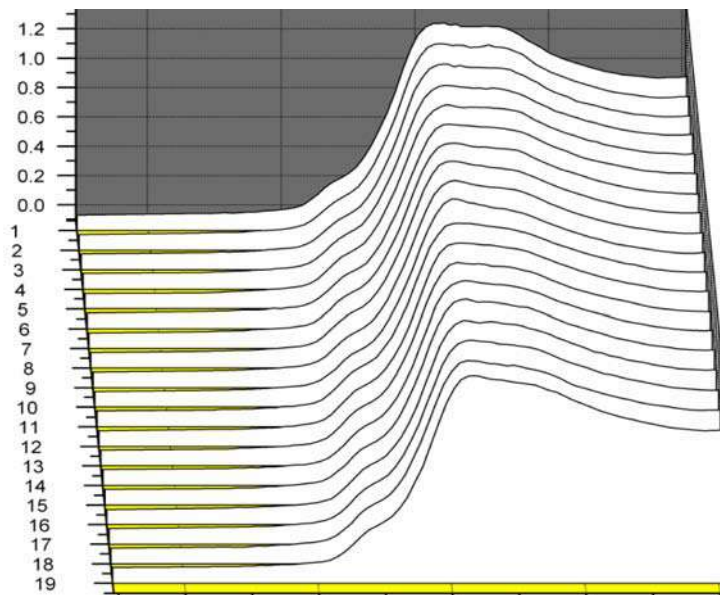
*Diagramme de diffraction de rayon X du bas vers le haut => de la nucléation à la cristallisation complète.*



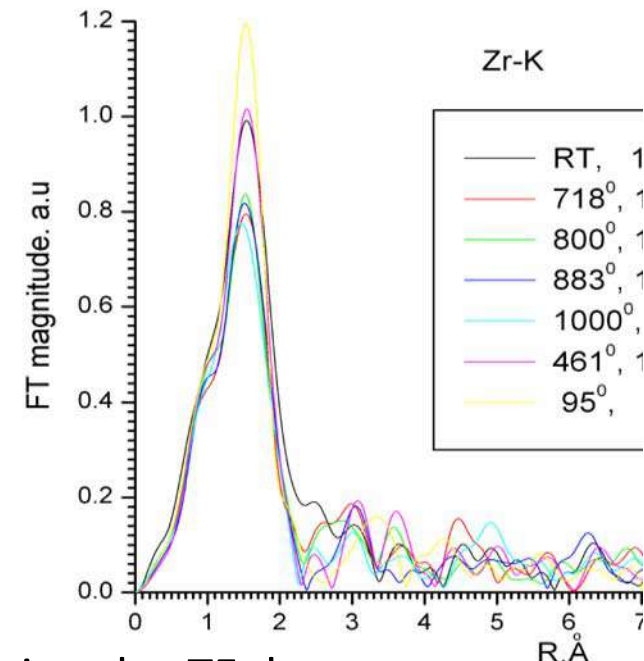
Évolution des spectres XANES au seuil K de Ti



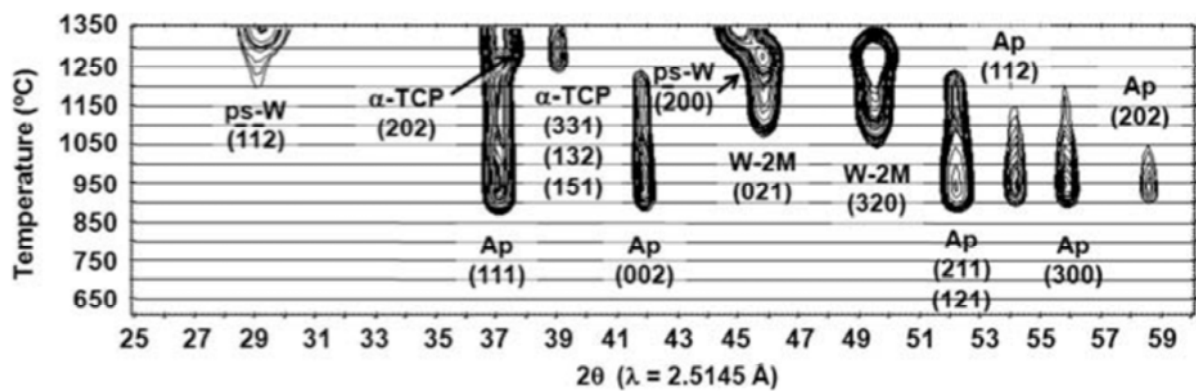
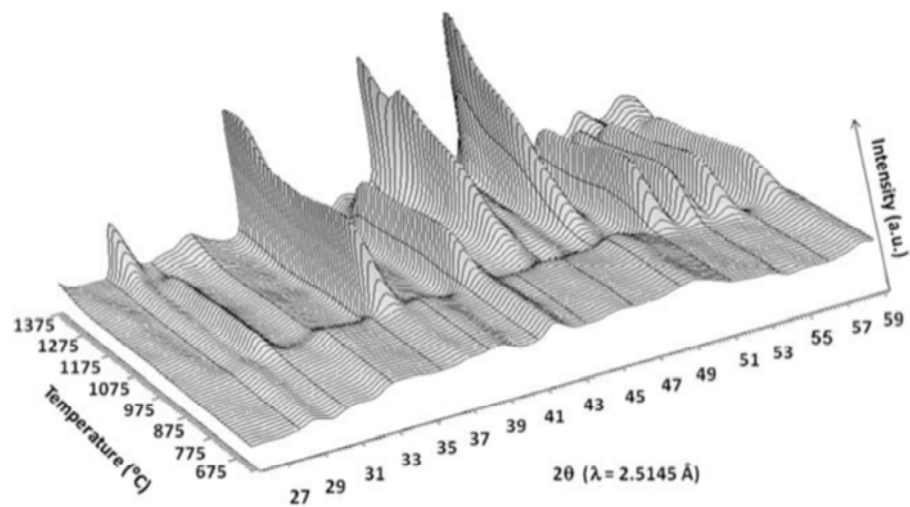
rampe de chauffe à 800°C (nucléation) et 1000°C (croissance).

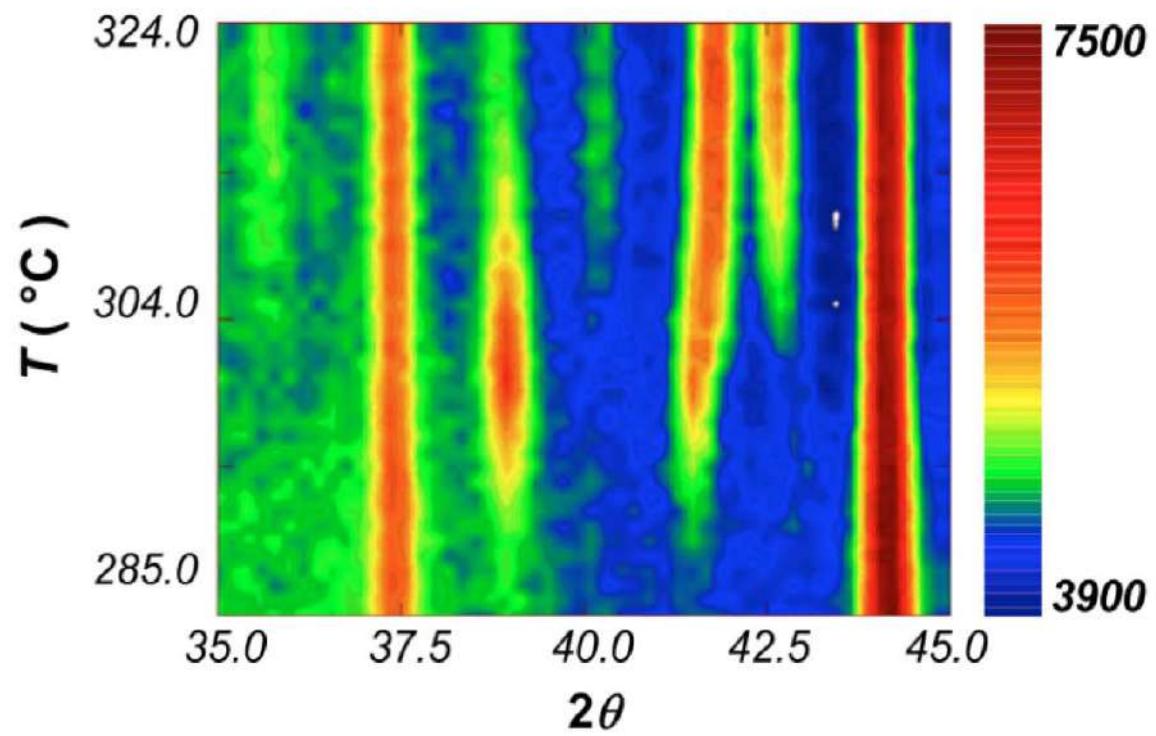
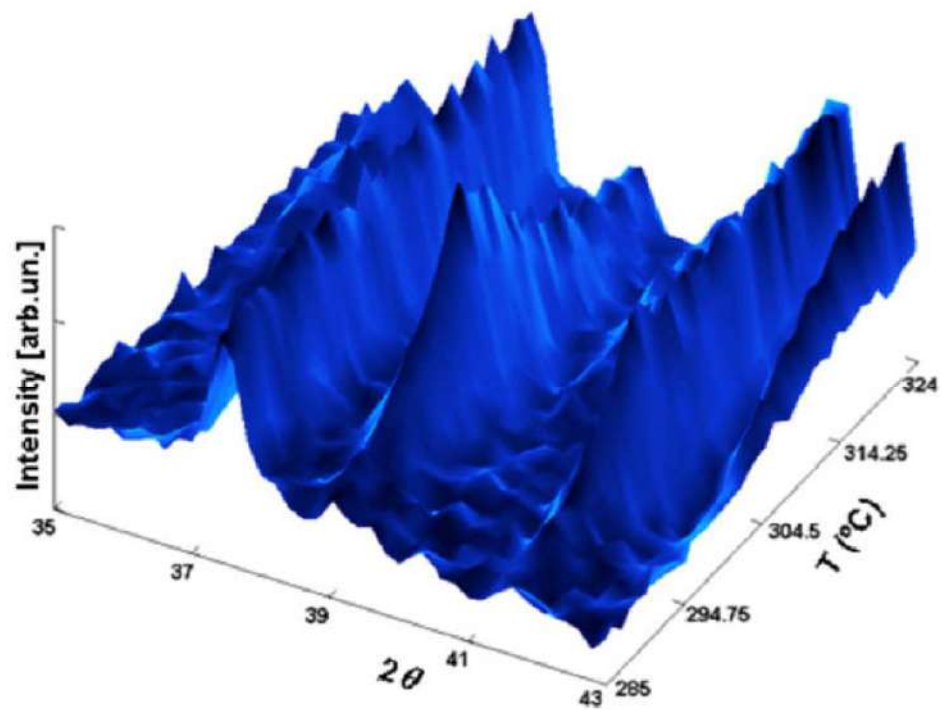


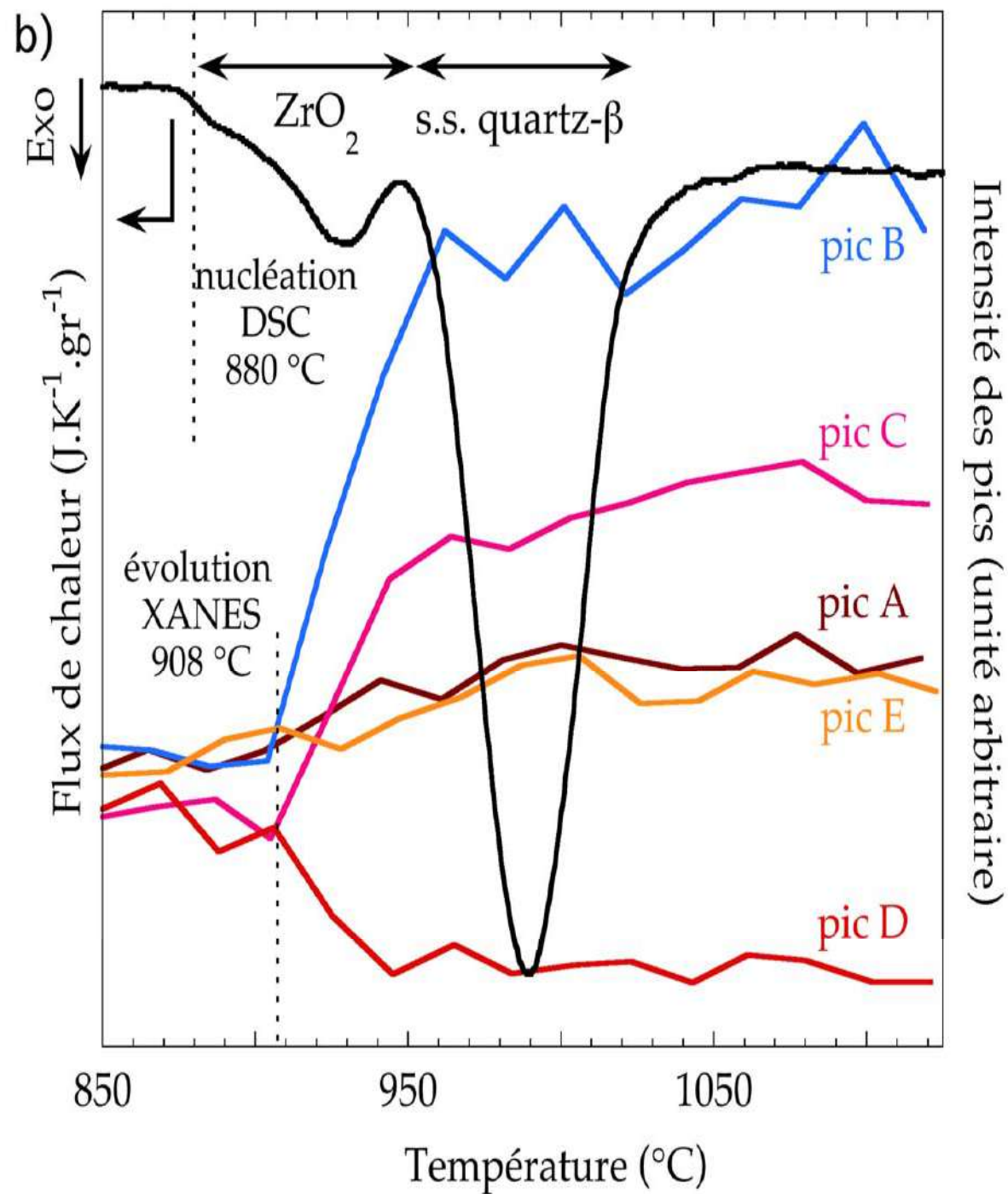
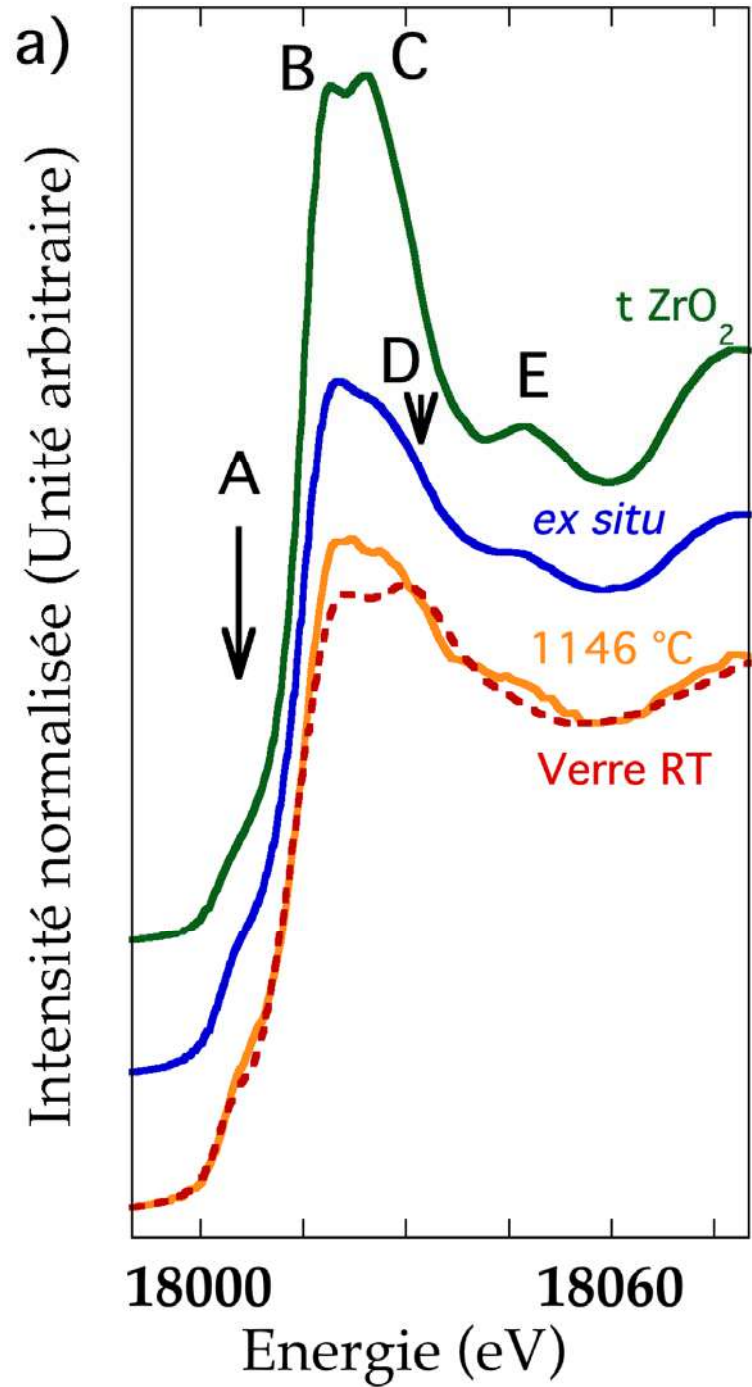
Évolution des spectres au seuil K de Zr



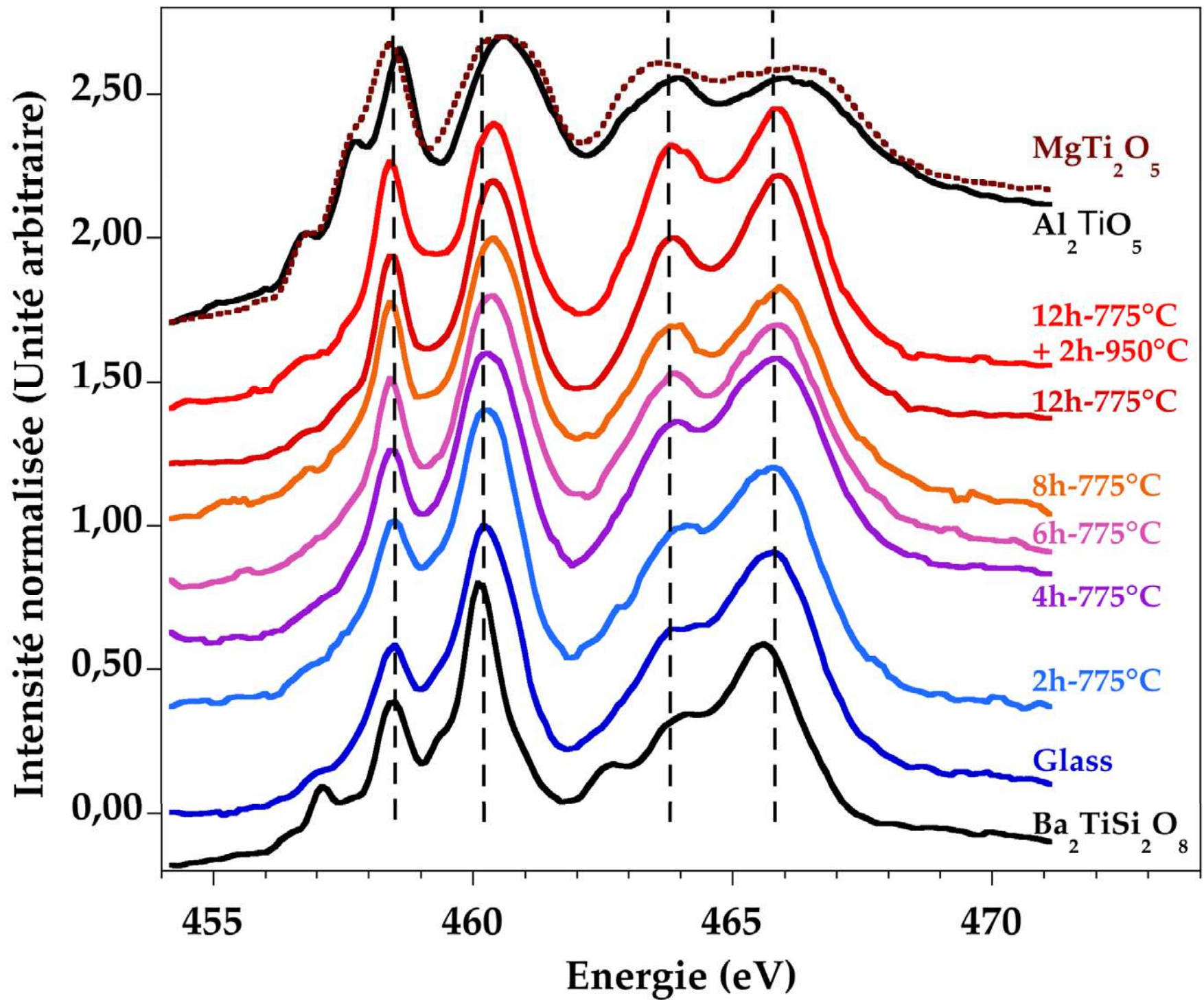
Évolution des TF des spectres au seuil K de Zr



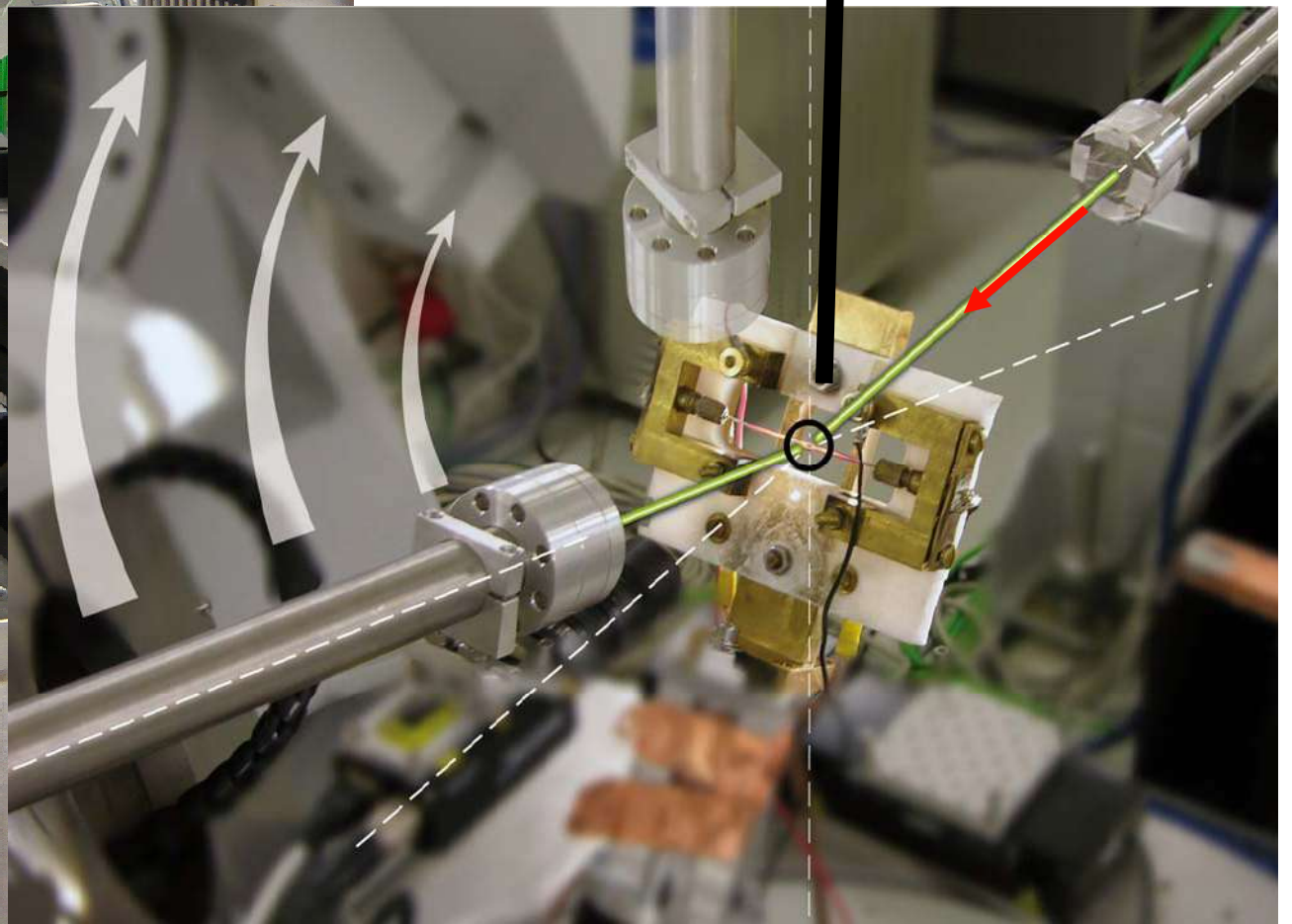
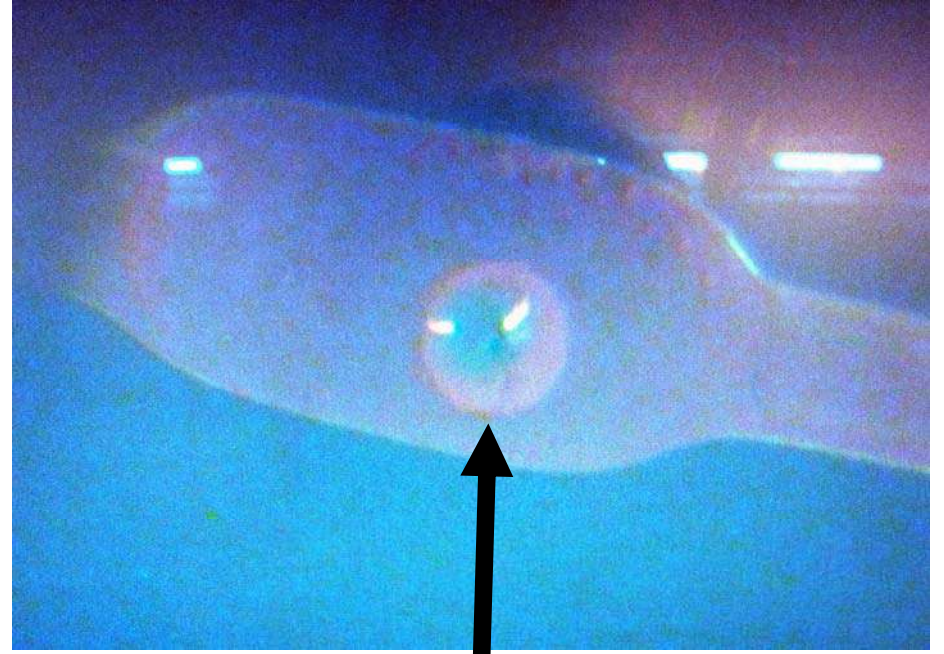
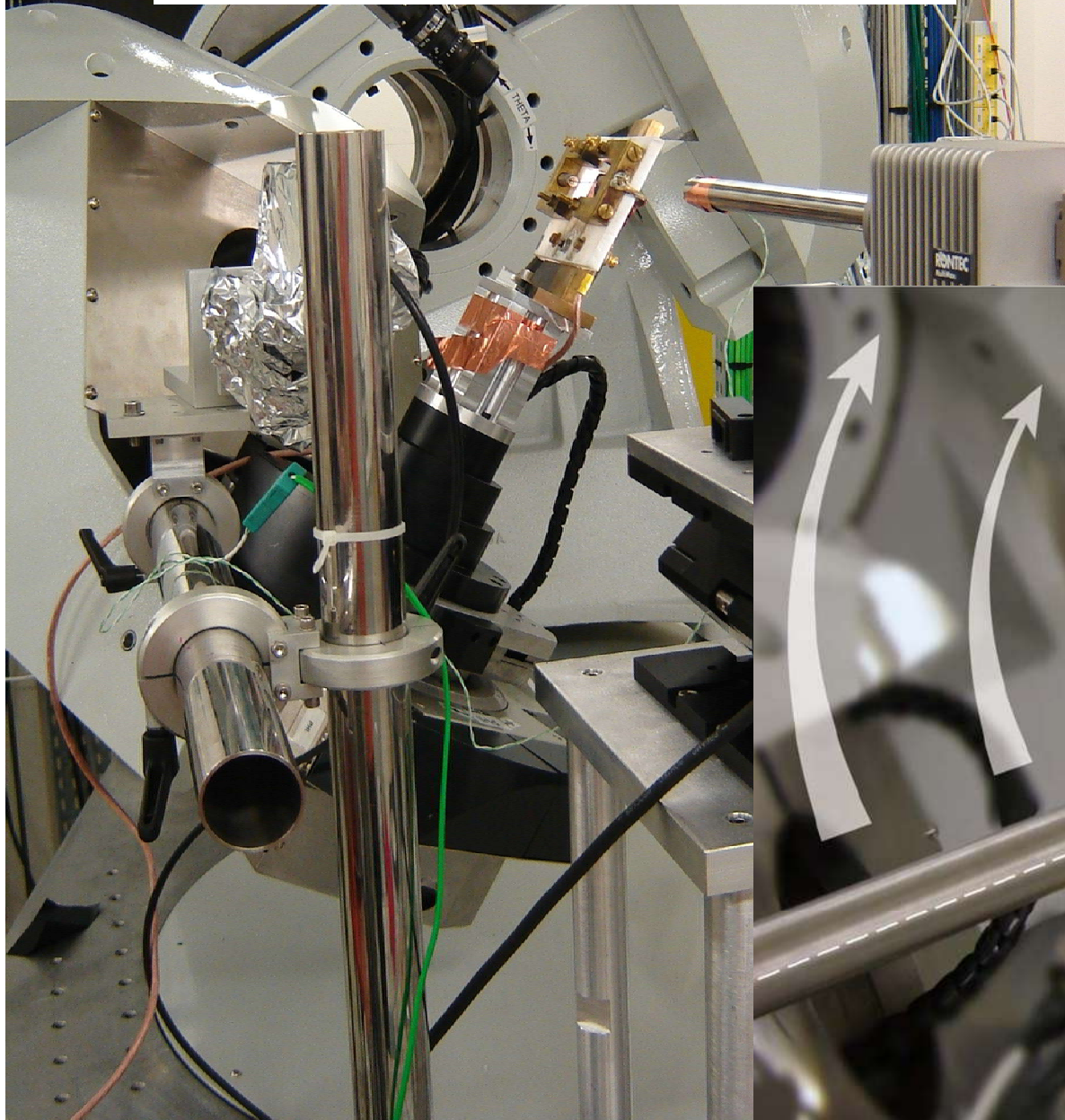


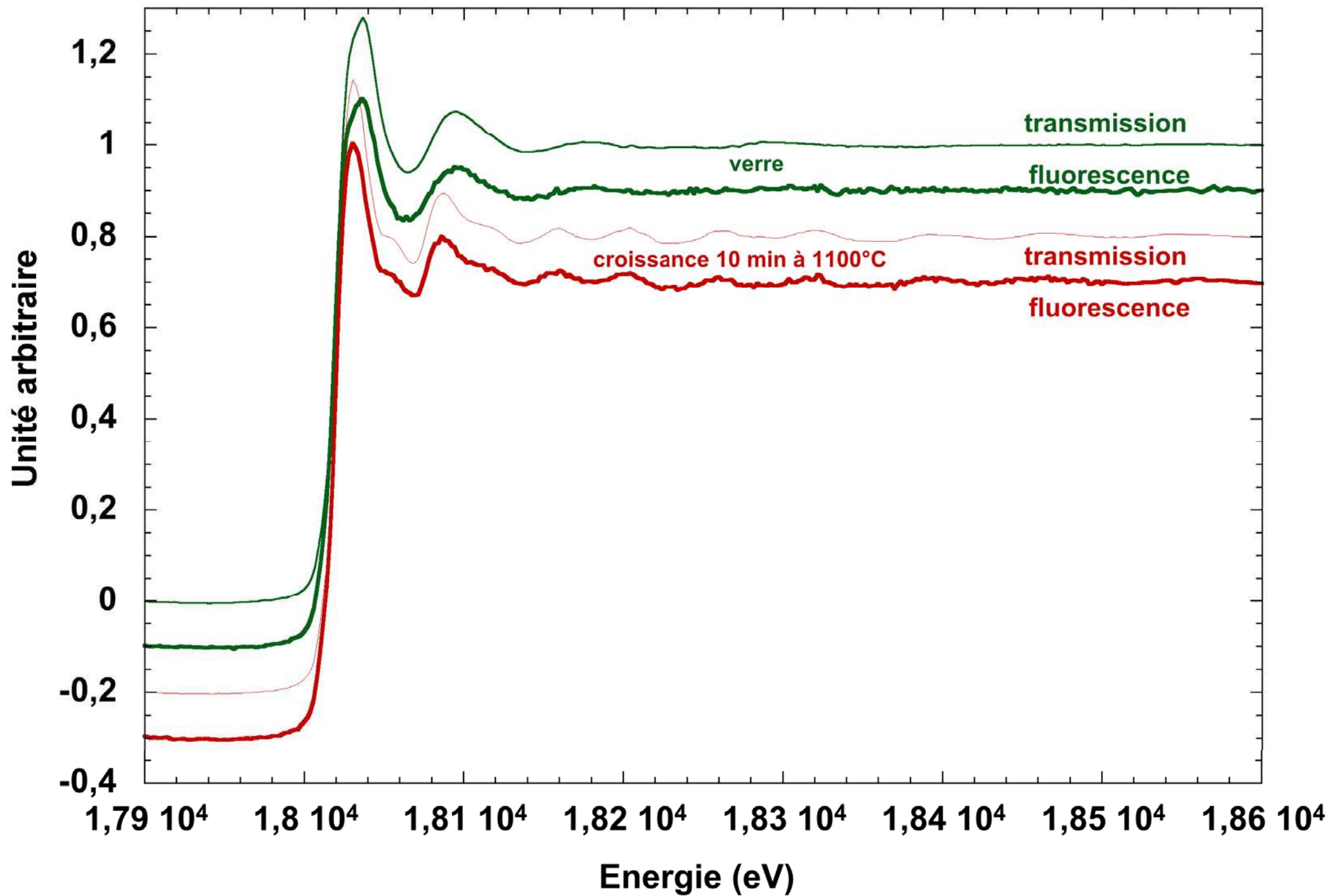




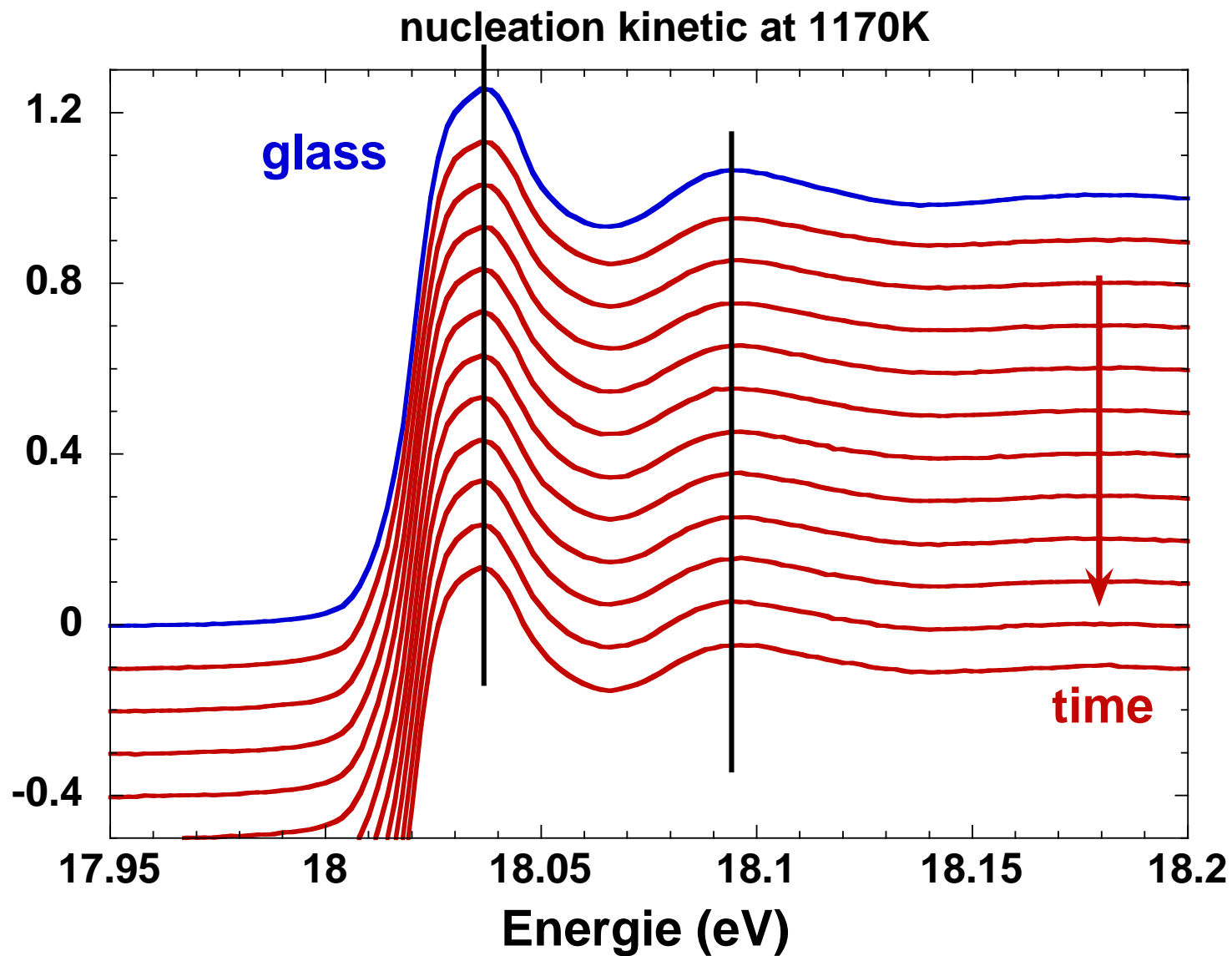


6 circles diffractometer  
on DIFFABS beamline  
'Soleil' synchrotron, France



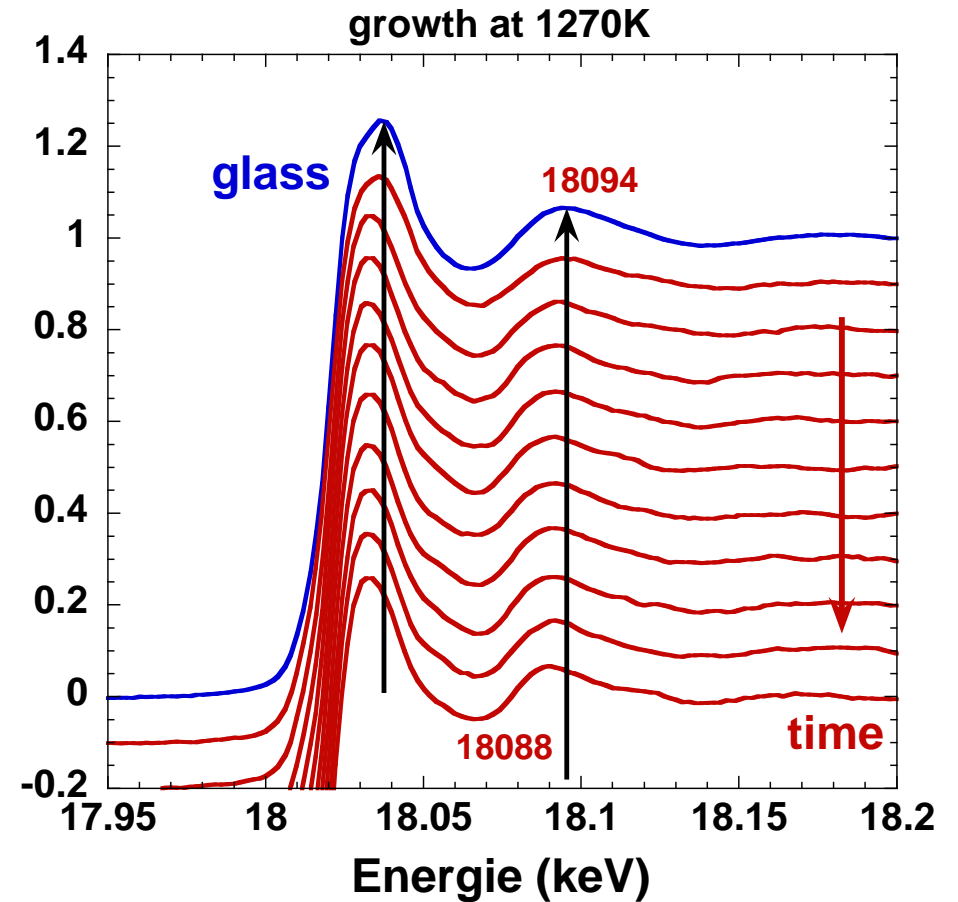
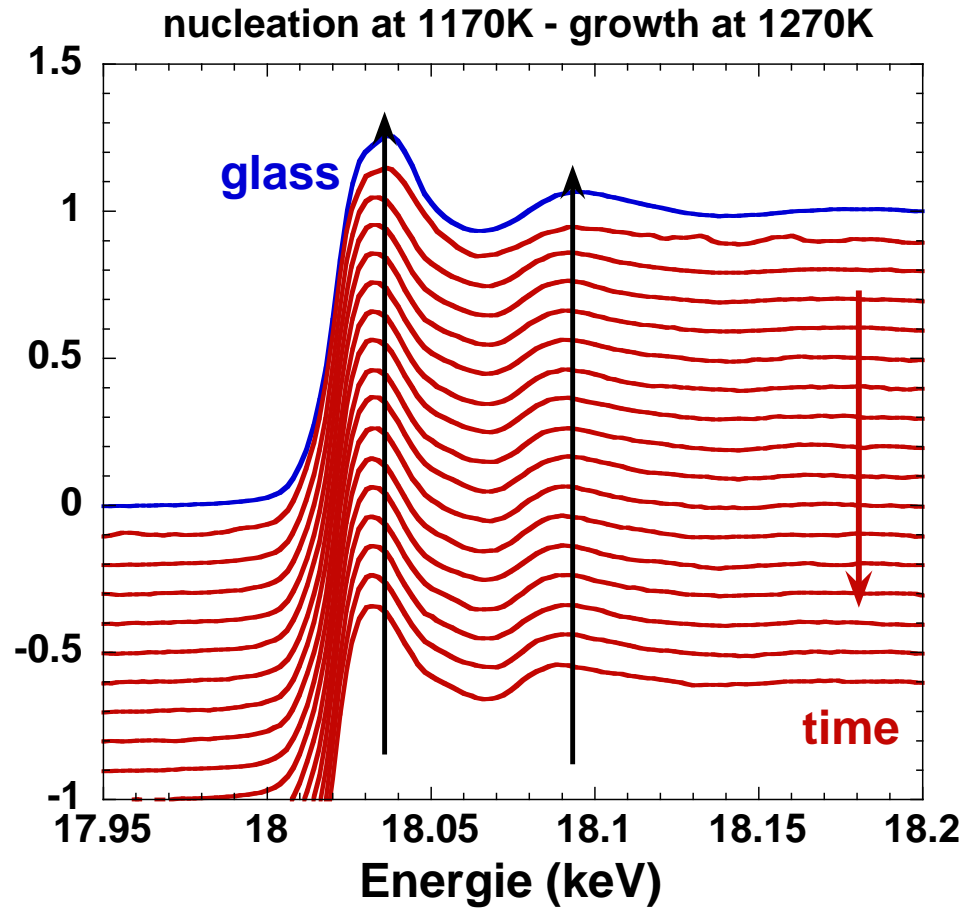


# EXAFS spectra at Zr K-edge



No major changes observed in XANES and EXAFS parts

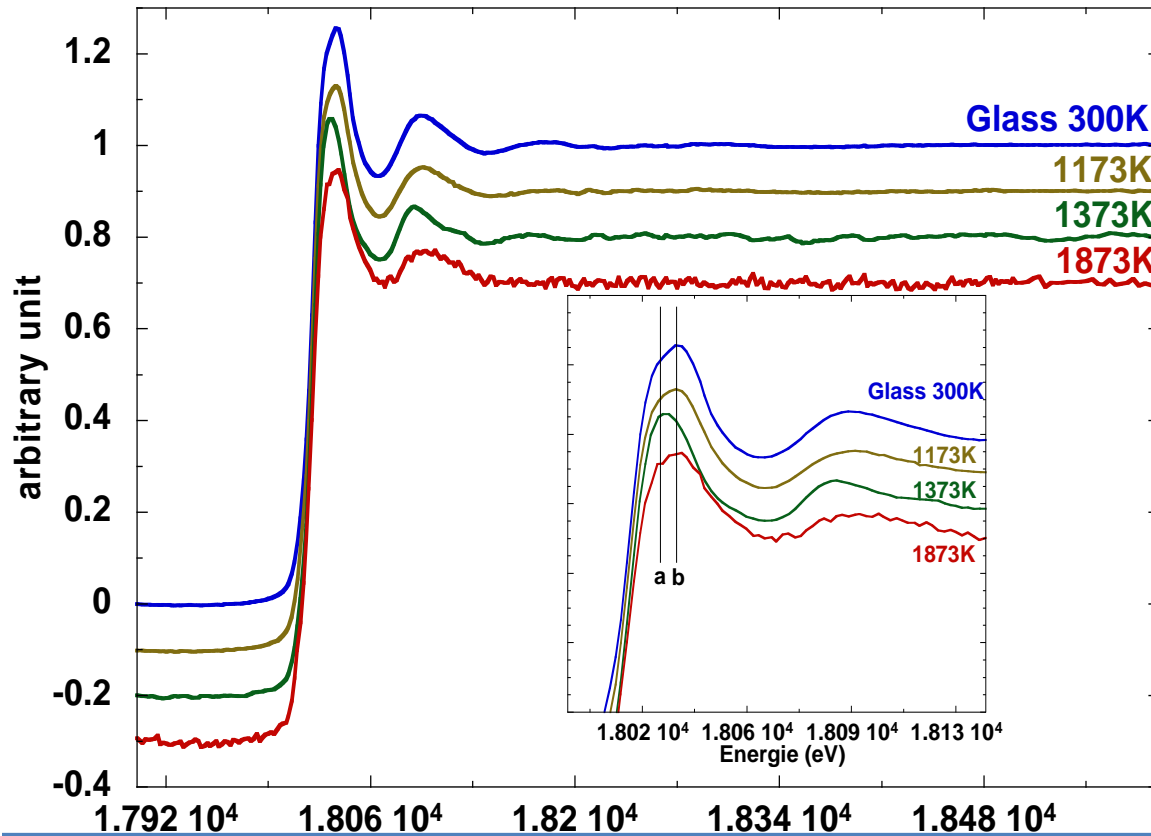
# Influence of annealing



No clear evidence of the influence of the nucleation stage on XANES

Changes visible in the very beginning of the annealing

Si (111) Absorption seuil K  
de Zr  
à haute température  
Mesure en transmission et  
en fluorescence

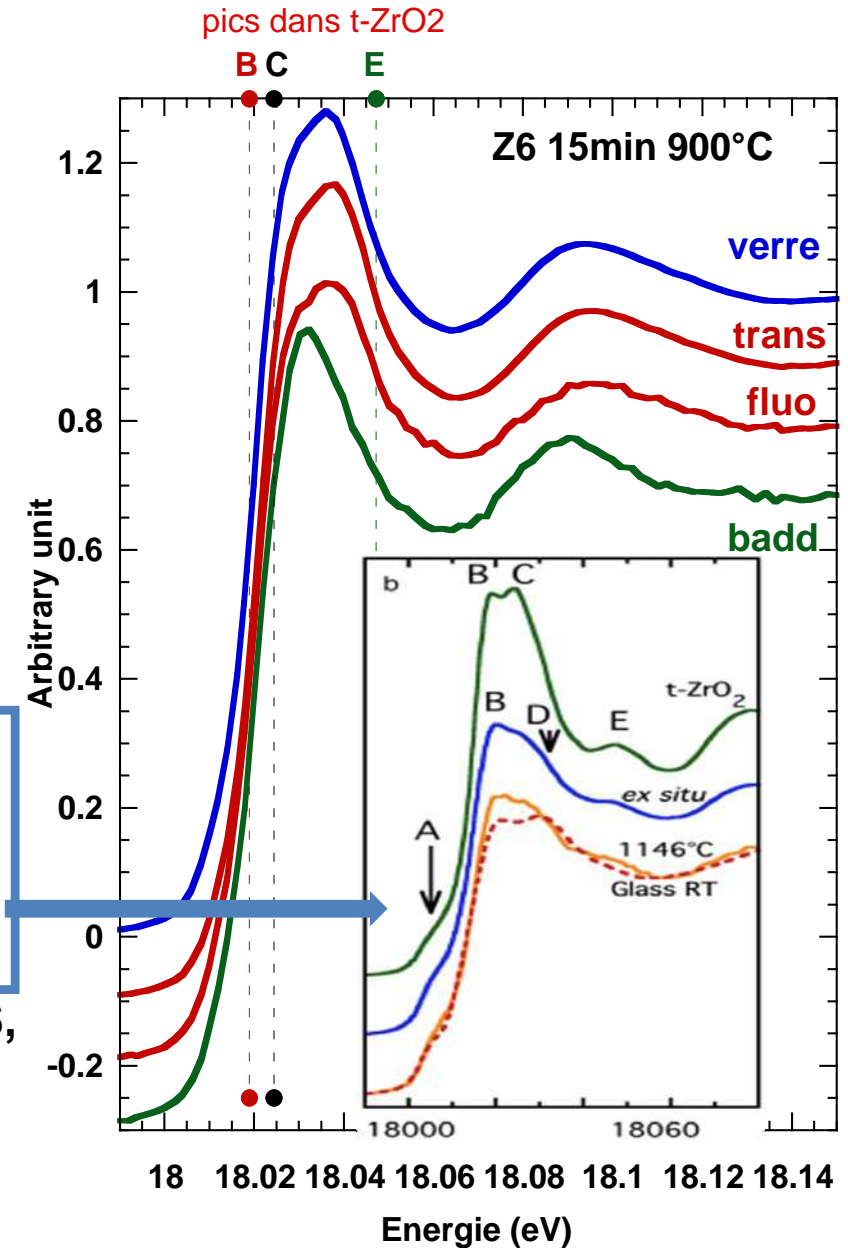


*In Situ* study of Nucleation of Zirconia in an MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> Glass

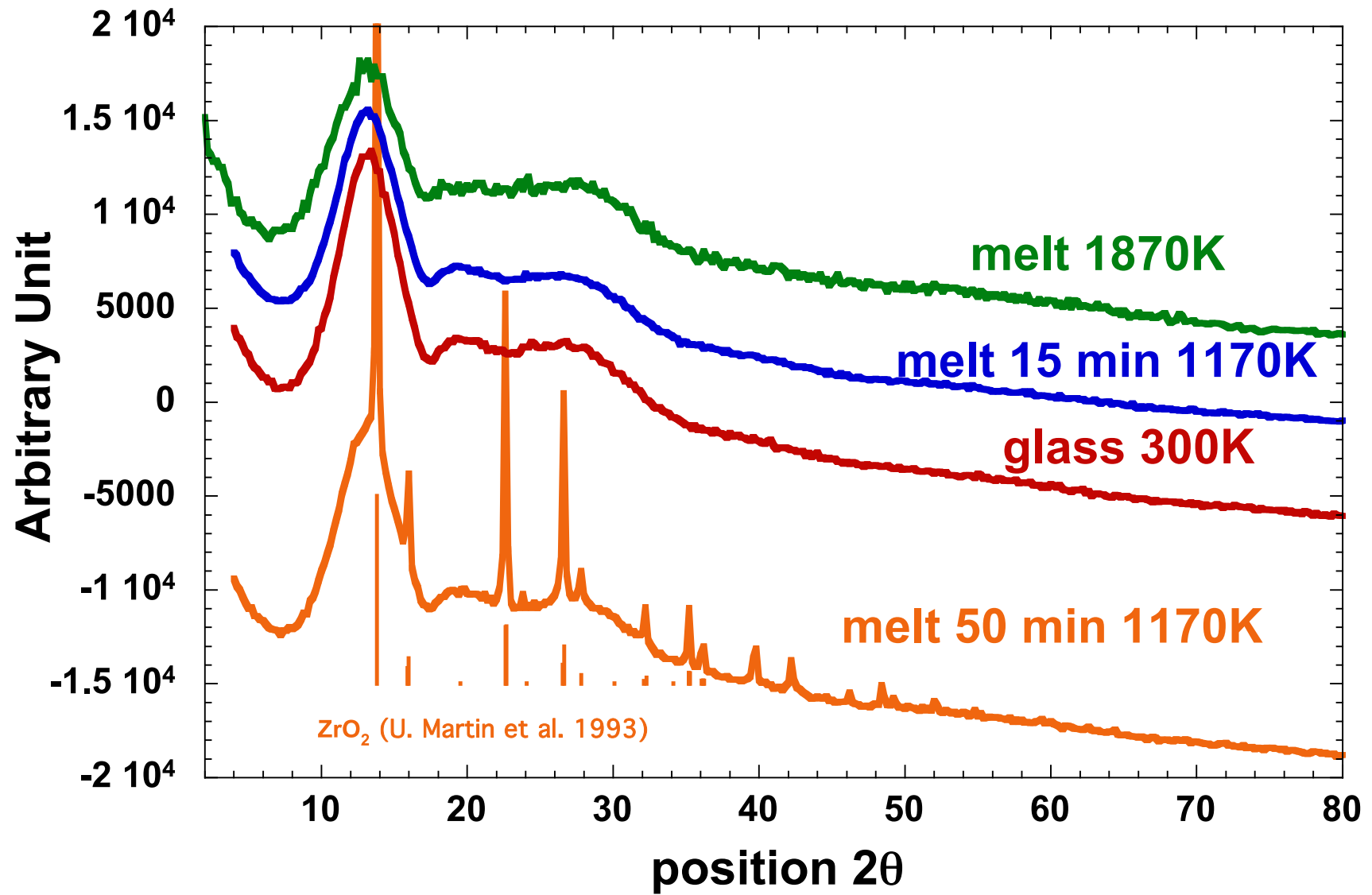
Olivier Dargaud,<sup>‡,§</sup> Georges Calas,<sup>\*,†,‡</sup> Laurent Cormier,<sup>\*,‡</sup> Laurence Galois,<sup>‡</sup> Cécile Jousseume,<sup>§</sup>  
Gilles Querel,<sup>†</sup> and Matthew Newville<sup>||</sup>

<sup>‡</sup>Institut de Minéralogie et de Physique des Milieux Condensés, Université Pierre et Marie Curie Paris 6,  
Université Paris Diderot, IPGP, CNRS UMR 7590, 75015 Paris, France

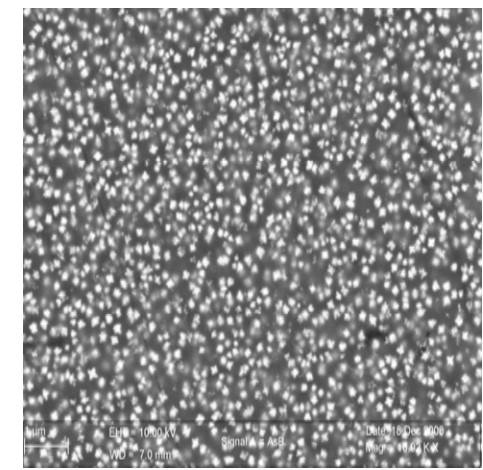
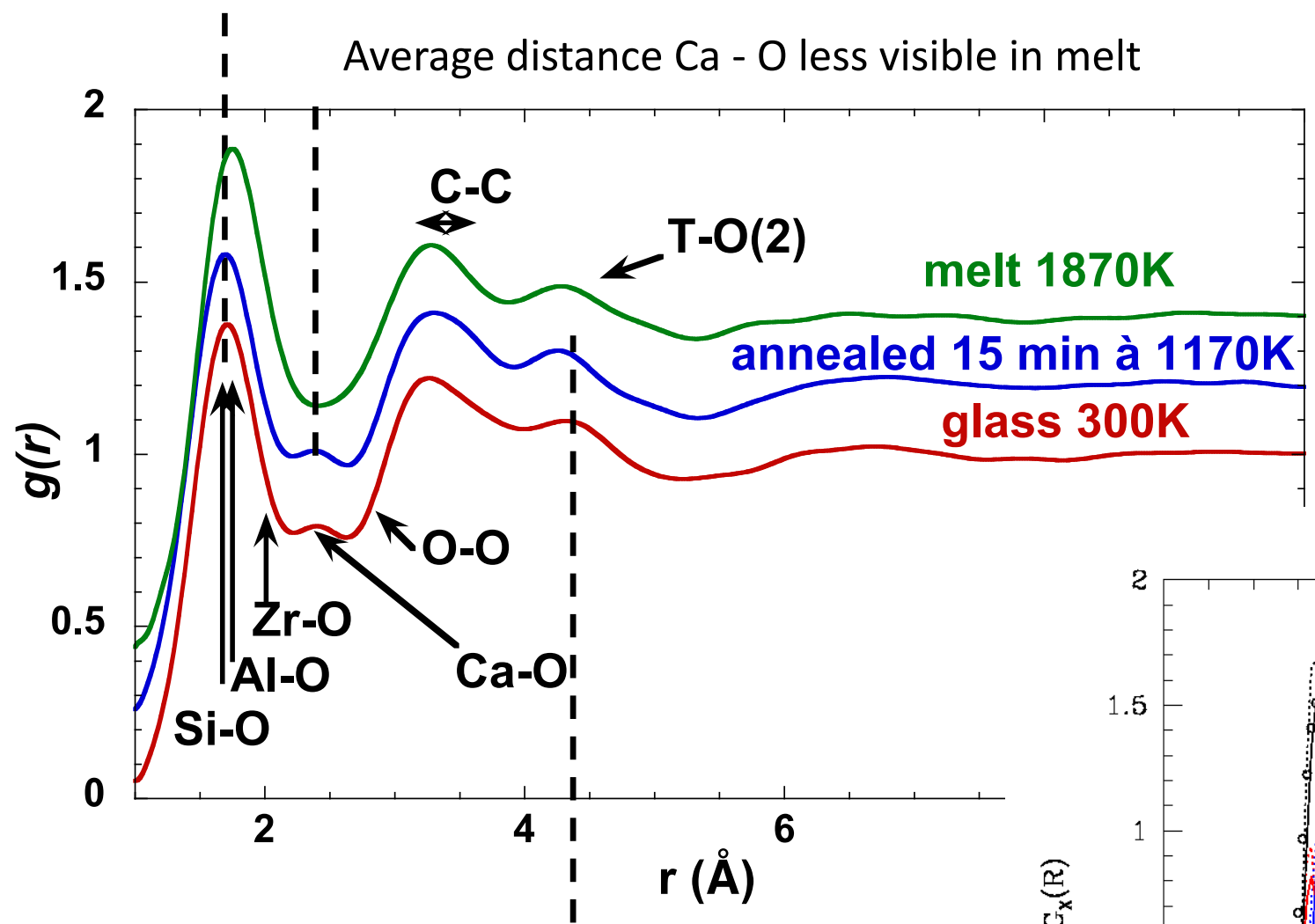
**Point B, C et E, Tetragonal ZrO<sub>2</sub> mais système MAS,  
cristallisation différente en fonction du système ...**



# X-Ray diffraction on melts and glass (17keV)

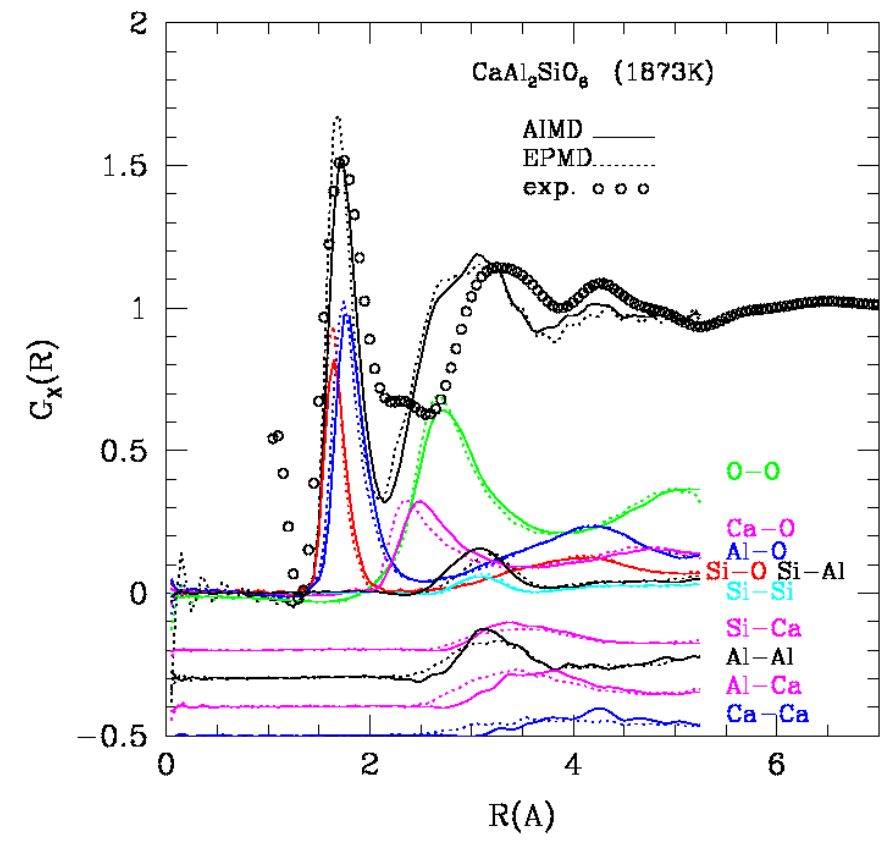


Expansion of the T - O distance



morphology of tetragonal ZrO<sub>2</sub>

Change in T - O distance





Seuil K de Ca

