JOURNÉES VERRE 2022
NICE & BIOT

21 – 23 Septembre 2022
Nice – Hôtel Aston La Scala
Biot – Salle Paul Gilardi

Prix distingué

L. Montagne

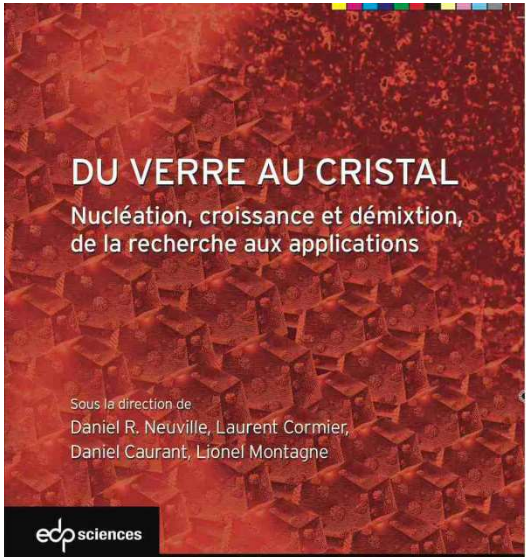
UNION
POUR LA SCIENCE
ET LA TECHNOLOGIE
VERRIÈRES

Université de Lille

Une belle distinction !

Bilan d'un partenariat fructueux !

- **Colloques**
  - 2014-2017 : 5 2010-2017 : 10
- **Ateliers**
  - 2014-2017 : 6 2010-2017 : 10
- **Ecoles thématiques**
  - 2014-2017 : 2 2010-2017 : 4
- **Organisation de symposia**
  - 2014-2017 : 1 2010-2017 : 3
- **Actions de formation/communication**
  - 2014-2017 : 2 2010-2017 : 4
- **Soutiens à des colloques (inscriptions doctorants)**
  - 2014-2017 : 13 2010-2017 : 20
- **Réunions…**
  - 2014-2017 : beaucoup 2010-2017 : TRES beaucoup



31 actions GdR-Verres – USTV en 8 années

GDR Verres
GDR 3338


Ecole thématiques CARGESE Mars 2017
GDR-Verres - USTV

LE VERRE Webinaires USTV

175 Abonnés • 45 Vidéos • 8.4K Vues

https://ustverre.fr/

Webinaire #15: Les verres phosphate

Modérateur : L. Cormier (IMPMC-CNRS)
Orateurs : L. Montagne (U. Lille), T..Cardinal (U.Bordeaux)

246 Vues • 4 Goûts

Webinaire #14 : Les verres de chalcogénure

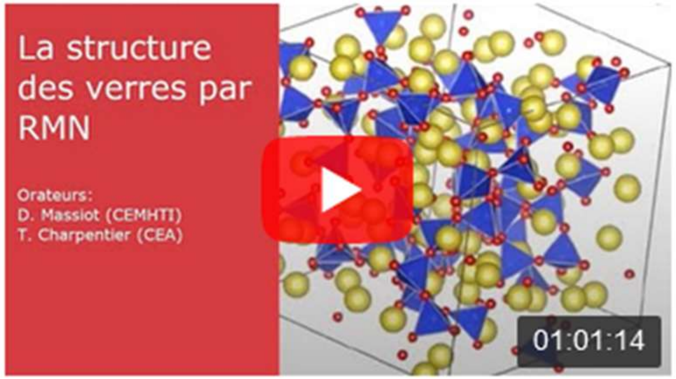
Modérateur : F. d'Acapito (ESRF)
Orateurs : A. Piarristeguy (ICG, U. Montpellier),...

159 Vues • 9 Goûts

Webinaire #13: Les bulles dans les verres

Modérateur : K. Burov (SGR)
Orateurs : A. Lechaczynski (Verrerie de Biot), F....

148 Vues • 3 Goûts



Webinaire #4: La structure des verres par ...

Modérateur : D. Neuville (IPGP-CNRS, U. Paris)
Orateurs : D. Massiot (CEMHTI-CNRS), T....

321 Vues • 6 Goûts

Webinaire #7: Fours et réfractaires

Modérateur : D. Neuville (IPGP-CNRS, U. Paris)
Orateurs : D. Coillot (Baccarat), B. Cissé...

1.1K Vues • 17 Goûts

USTV - Journées Verre de Nice

Phosphate glasses :
- some aspects of their chemistry and related applications
- structure of ultrathin phosphate glasses

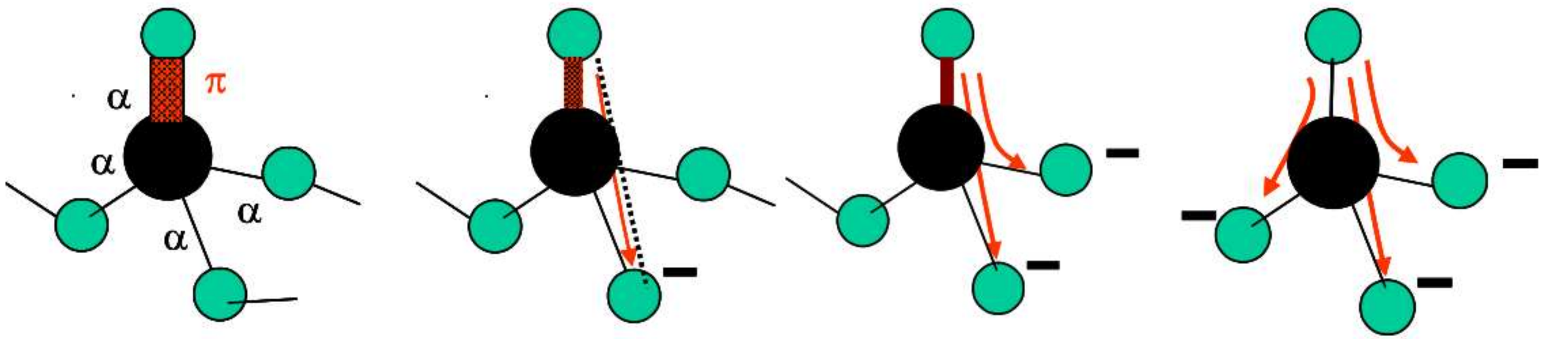
L. Montagne

Université de Lille

UCCS Unité de Catalyse et Chimie du Solide

The starting point…

- P [Ne] $3s^2$ $3p^3$ => sp^3 hydridization
- P^{5+}
- Tetrahedral P coordination => presence of π electrons on P-O bonds
- P=O d=0,145nm, P-O-P d=0,15 à 0,16 nm
- Some delocalization of π electrons, depending on the the number of POP



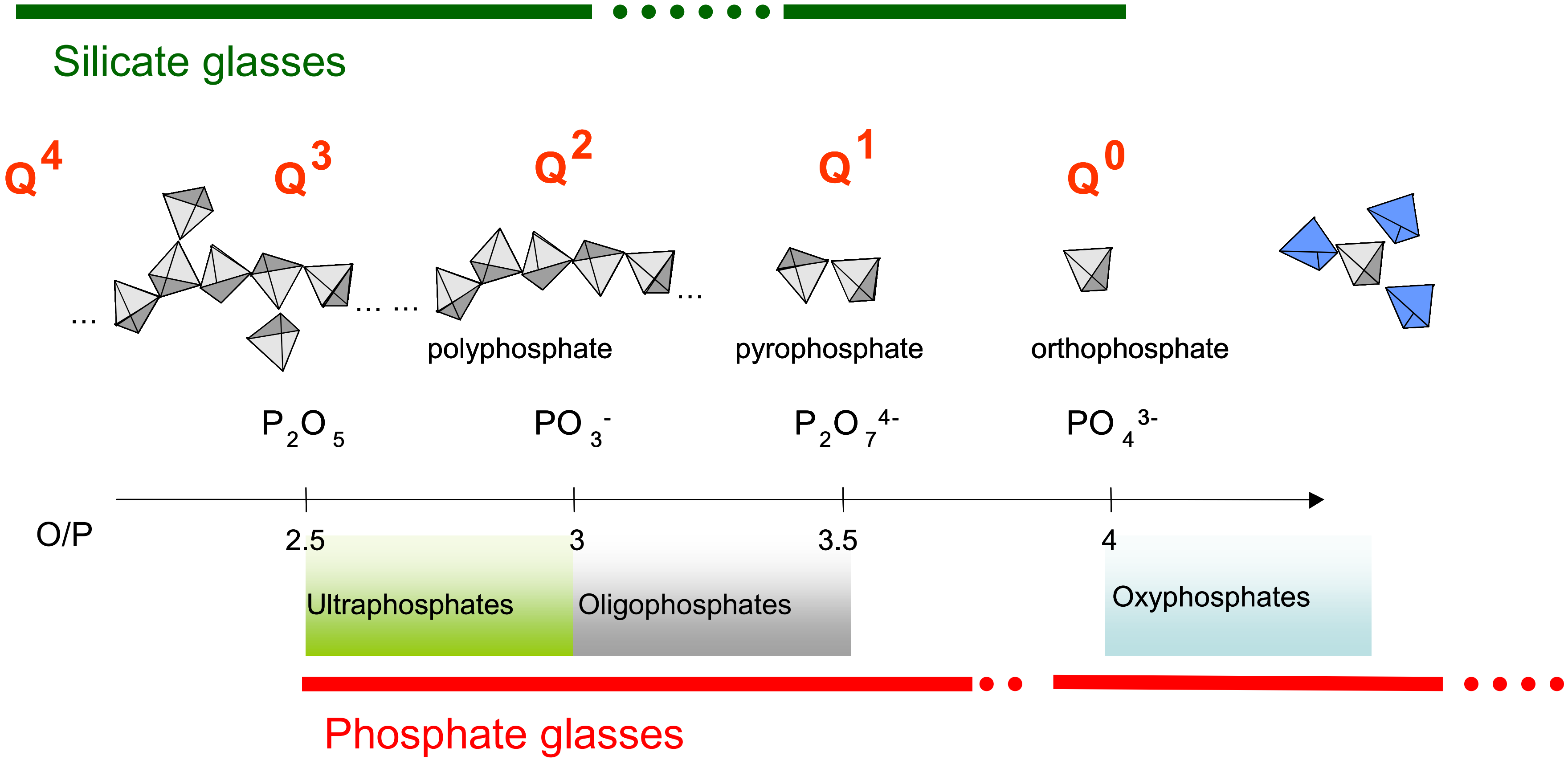
Q^3 Q^2 Q^1 Q^0

Videau, Le Flem (2010)

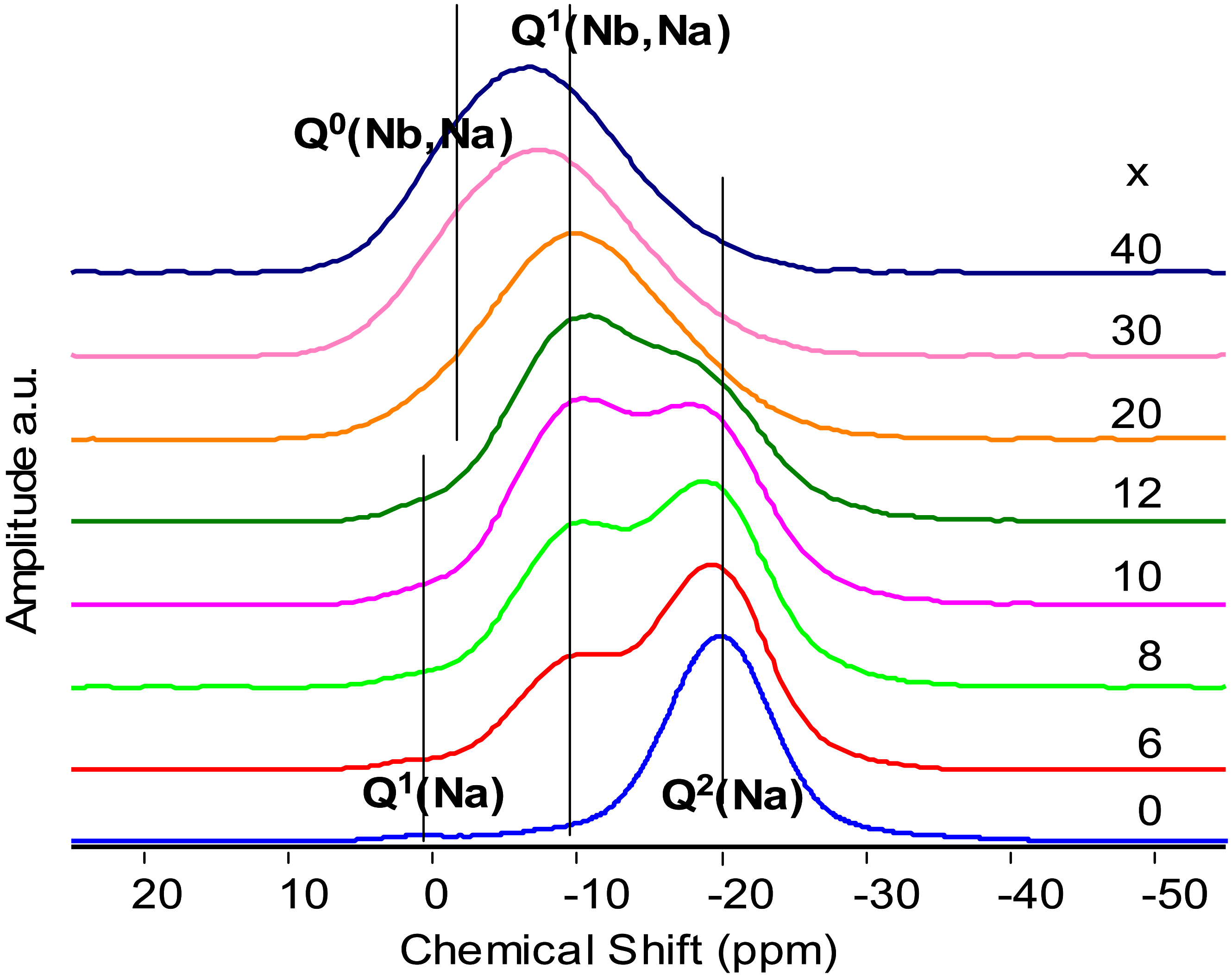
Consequence 1:

- silicates : Q^0 to Q^4, phosphates Q^0 to only Q^3

=> Phosphate glasses are often much less polymerized than silicate glasses



^{31}P of phosphate glasses : Q^n species



^{31}P NMR of **xNb_2O_5-(100-x)($xNaPO_3$) glasses**

Consequences of low network connectivity

=> Low Tg values

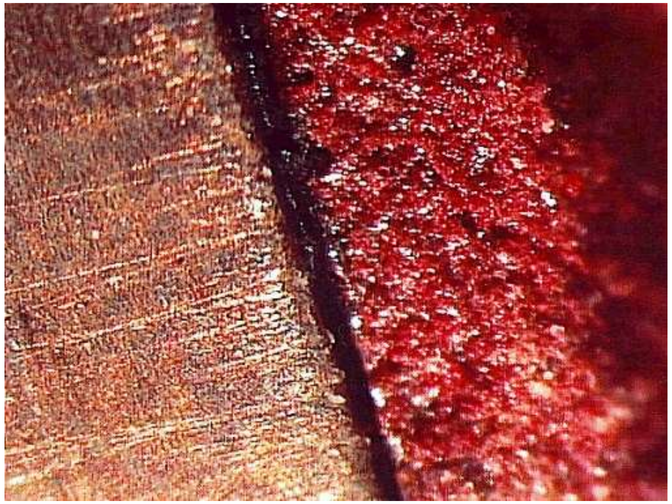
- Typical values between 250 and 400°C
- Tg values down to RT for fluorophosphate glasses !

=> Large coefficient of thermal expansion (10 to $25.10^{-6}K^{-1}$)

- Applications for sealing to Al alloys in electronic packaging

=> But… *Low chemical durability !*

Al, Cu alloys, CTE#$25.10^{-6}ppm.K^{-1}$



Sealing of BiMeVOx to Stainless steel (SOFC fuel cells)

CTE#$16\text{-}17.10^{-6}ppm.K^{-1}$

Bi_2O_3 highly reactive

Formulation of Bi_2O_3-V_2O_5-P_2O_5 glass

Low chemical durability may be usefull?

- Phosphate glass fertilizers
- Slow release of oligo-elements (Mn, Cu)

Glass code	Mol %			
	P_2O_5	K_2O	CaO	MgO
	Set B			
B-1	33.33	33.3	11.1	22.2
B-2	36.84	31.6	21.1	10.5
B-3	40.00	30.0	20.0	10.0
B-4	42.86	28.6	19.0	9.5

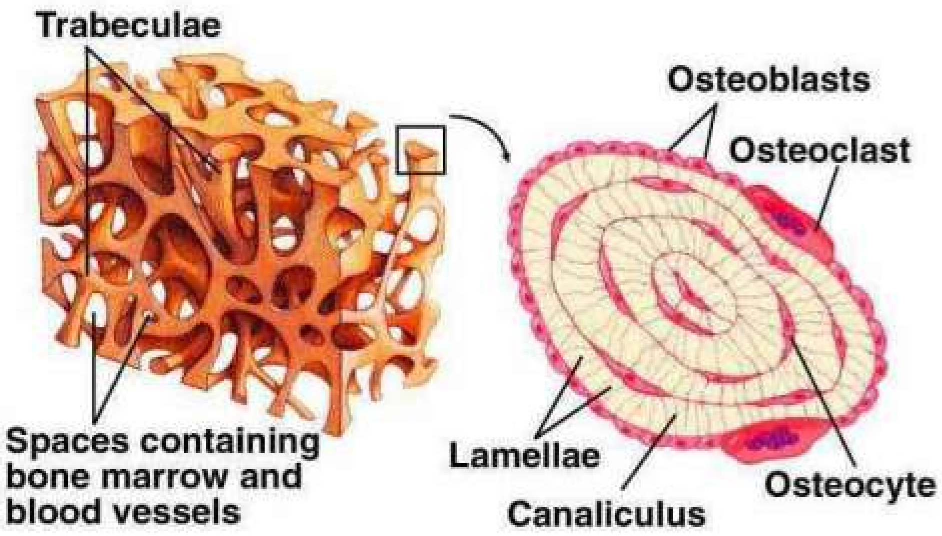
	CuO	MnO_2	MoO_3	Fe_2O_3	ZnO	CoO	S	B_2O_3
B-3M1	0.61	0.61	0.61	0.61	0.61	0	0	0
B-3M2	0.025	0.051	0.024	0.012	0.024	0.026	0.025	1.44

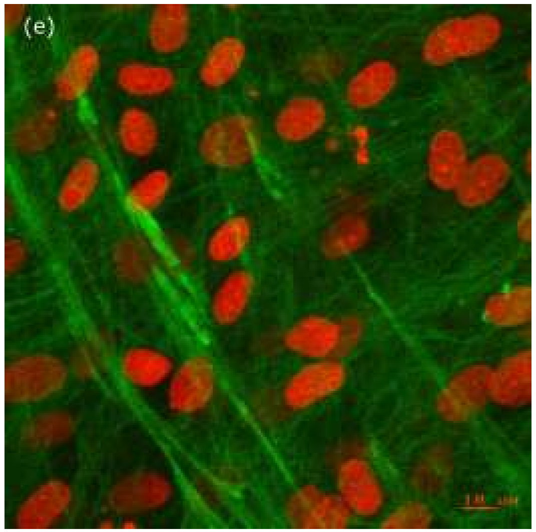
Ivandelko Völkenrode (2007)

Low chemical durability may be usefull?

Phosphate glasses as biomaterials

- Bone is made of apatite = calcium phosphate
- Hench's bioglasses : Ca, Na silicophosphates
- Vogel et al : Ca, Fe, Na phosphate glass-ceramics (machineable)
- Knowles : Na, Ca, Ti phosphate
- Good biocompatibility
- ***Control of dissolution rate is a key issue***





Knowles Acta Biomaterialia (2012)

Low chemical durability may be usefull?

Calgonit Diamond® : slow release of zinc phosphate protects glasswares in dishwasher (pH buffering and surface adsorption)

Consequence 2 :

- Compare z/a^2 (valence/ionic radius) of :
  - P^{5+} : $2{,}16.10^{20}$ m^{-2}
  - Si^{4+}: $1{,}54.10^{20}$ m^{-2}
  - B^{3+}: $1{,}39.10^{20}$ m^{-2}

  - Means that P_2O_5 is a strong Lux & Flood acid:
    - $P_2O_5 + O^{2-} \Leftrightarrow 2PO_3^-$
    - *e.g.* $MO + P_2O_5 \Leftrightarrow M(PO_3)_2$

  => Strong reactivity with other oxides
    - FluoX pearls
    - Mixed-network glasses…

Consequence 2: large dissolution capacity in phosphate network

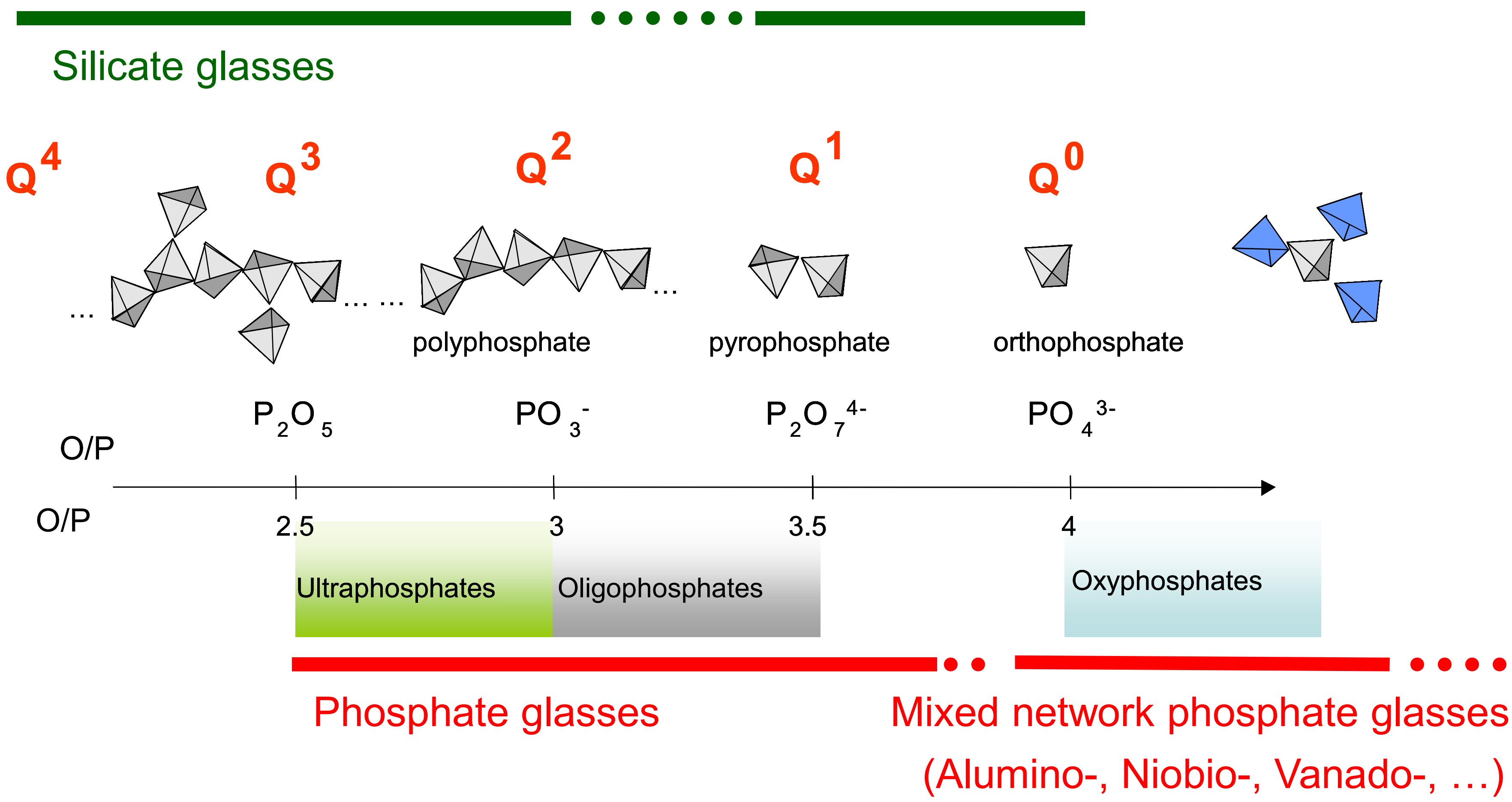
Nd-doped Ba metaphosphate (Q[2] glasses)

- 3000 glass slabs :
  - Index uniformity to <±0.000001
  - Free of inclusions and bubbles larger than 100um
  - Residual hydroxyl content <100ppmw
  - Platinum particle free
  - Free of all detectable striae
  - Low 1054nm absorption of <.19% per cm thickness

⇒ High Nd content without clustering effect

Beamlet 18 liter rare earth doped phosphate glass amplifier slab

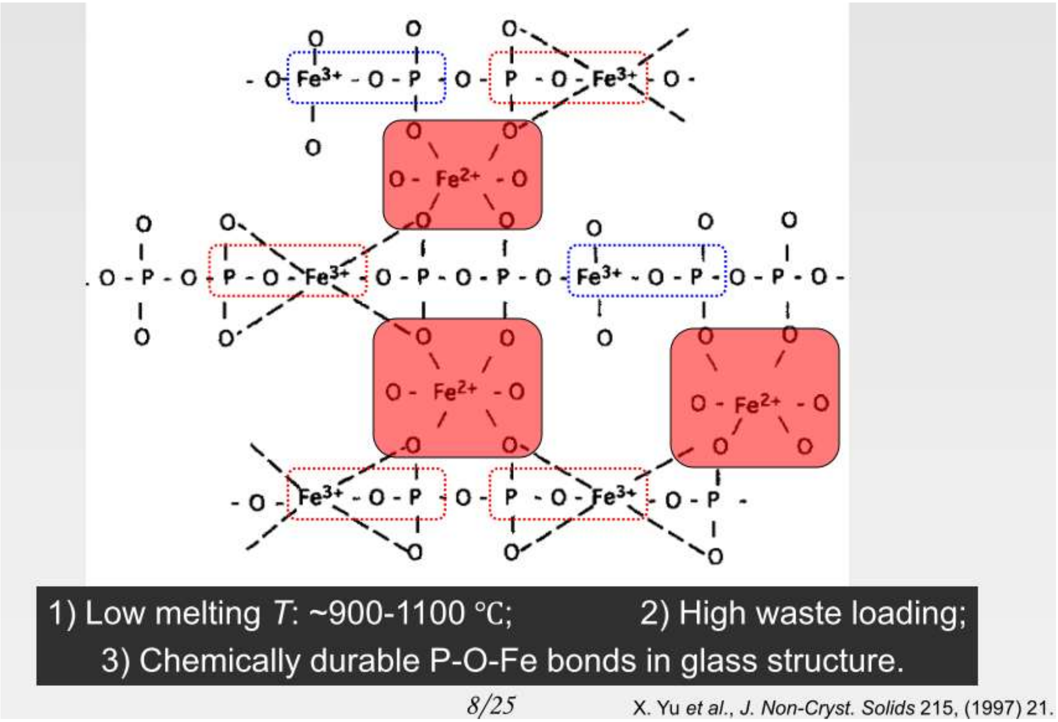
Consequence 2: large dissolution capacity in phosphate network
=> Mixed network glasses are easy to prepare from phosphates

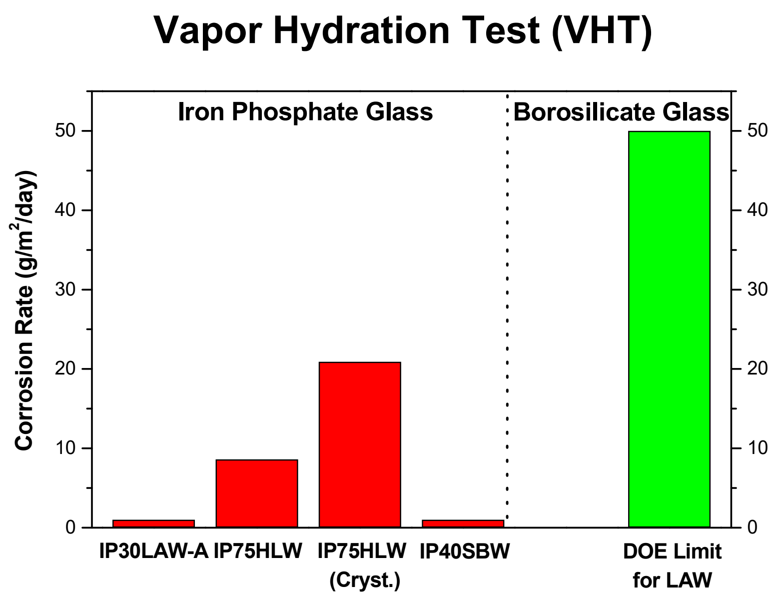


Mixed-network Phosphate glasses are durable !

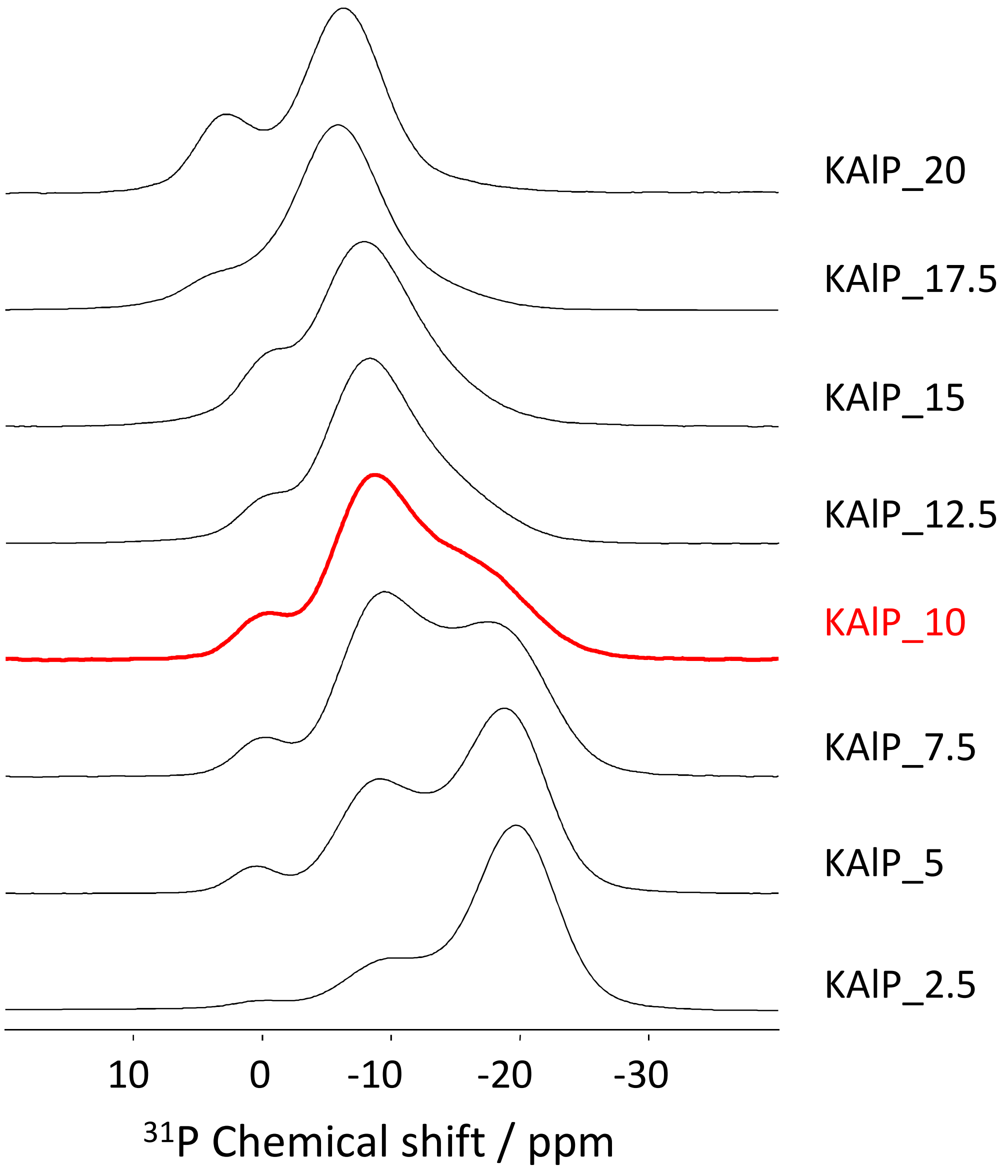
- Alternative solution to borosilicate glasses for special wastes
  - Higher waste loading
  - Larger solubility of chromium, molybdenum
  - Lower melting T : less volatilization of sulfur, iodine
- 70' : USSR: Mamoshin, Stefanovski: aluminophosphate glasses
- 80': USA: Sales and Boatner : Pb-Fe phosphate glasses
- 90': USA: Day : Fe phosphate glasses

iron phosphate waste form containing 40 wt% of simulated nuclear waste.
https://mo-sci.com/





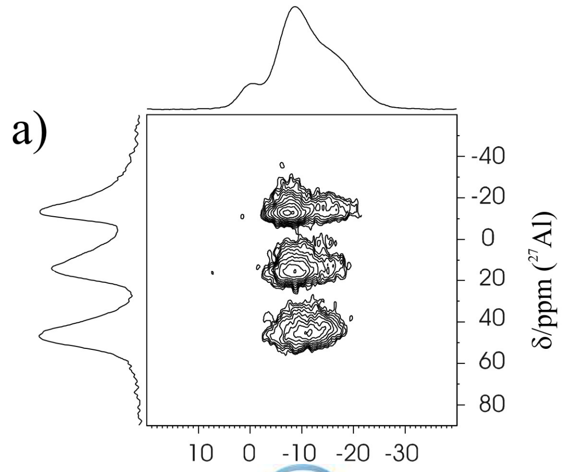
Mixed network : alumino-phosphate glasses



- Poor resolution (overlapping of several resonances)

- Number of sites ?

- No accurate structural model can be obtained from the 1D results => 2D NMR toolbox

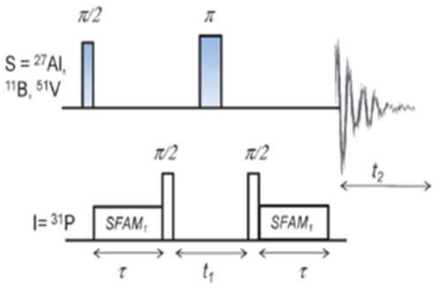


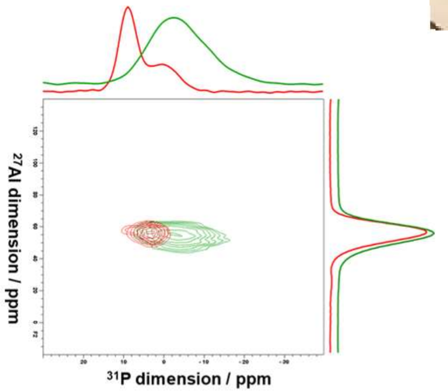
Mixed network : alumino-silico-phosphate glasses

CORNING

Phosphorus-aluminium interactions driving crystallization in aluminosilicate glass-ceramics: an NMR approach of an industrial question

Better nucleation enables saving energy in cristallization process





Thesis: Pauline Glatz,
Co-direction Laurent Cormier,
Monique Comte
UPMC-ULille-CORNING, CIFRE 2018

Phosphate glasses: applications are related to network polymerization

Phosphate glasses

Mixed network phosphate glasses

- *Water softening*
- *biomaterials*
- *sealing glasses*
- *Photonic glasses, laser glasses*
- *Electrolyte glass*
- *Anti-oxidation coatings*
- *Nuclear waste vitrification*

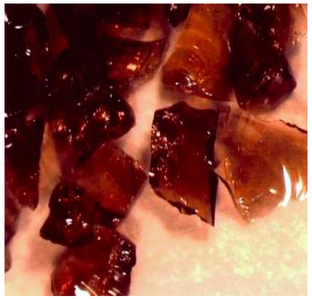
Water softening

Biomaterials

Sealing glasses

Laser glasses

Waste storage



Anti-oxidation coating

Phosphate glasses: applications are related to network polymerization

Phosphate glasses

Mixed network phosphate glasses

-*Water sof*

- *biomateria*

- *sealing gla*

- *Photonic g*

- *Electroly*

- *Anti-oxid*

- *Nuclear wa*

Webinaire #15: Les verres phosphate

Modérateur : L. Cormier (IMPMC-CNRS)
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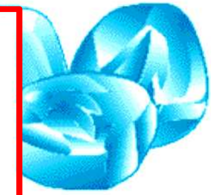
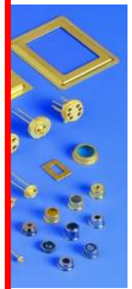
246 Vues • 4 Goûts

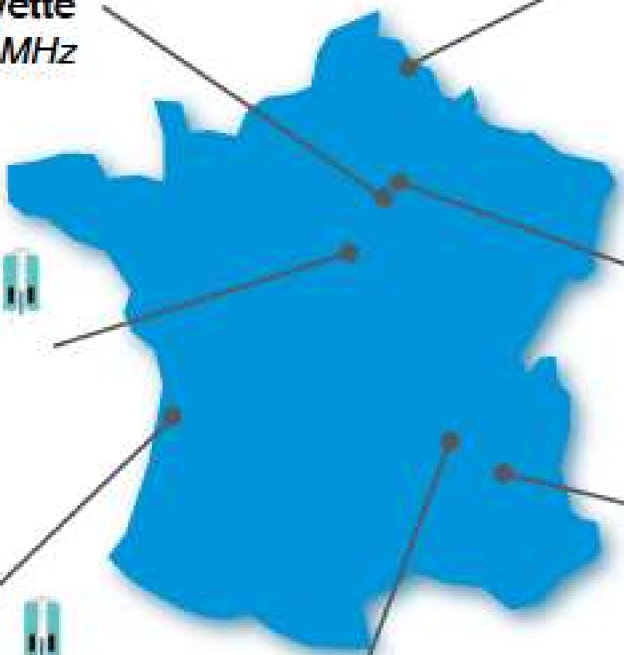




ating

French high-field NMR-EPR-MS infrastructure

infranalytics



Eric Guittet
ICSN, **Gif/Yvette**
950 MHz

Olivier Lafon
UCGS-UGSF, **Lille**
800 & 900 MHz
Université de Lille 1

Frank Fayon
CEMHTI, **Orléans**
750 & 850 MHz WB

Geoffrey Bodenhausen
LBM, **Paris**
800 MHz WB
UPMC
ENS

Antoine Loquet
CBMN-IECB, **Bordeaux**
800 MHz
Inserm
IPB
université de BORDEAUX

Bernhard Brutscher
IBS, **Grenoble**
950 MHz
cea
Université Grenoble Alpes

Guido Pintacuda
ISA-CRMN, **Lyon**
800 & 800 WB DNP & 1000 MHz
ENS DE LYON
Lyon 1

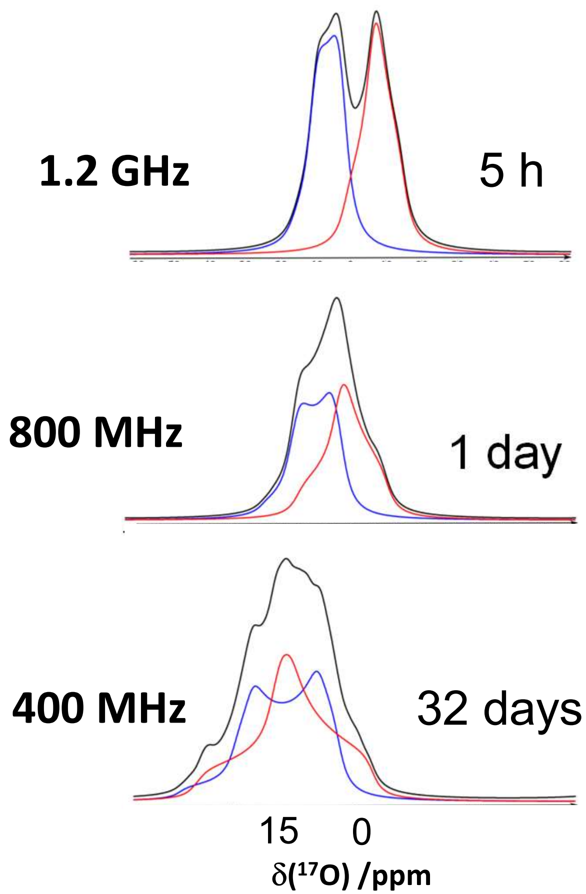
1.2 GHz NMR open facility !

https://infranalytics.fr/intranet/deposer-un-projet

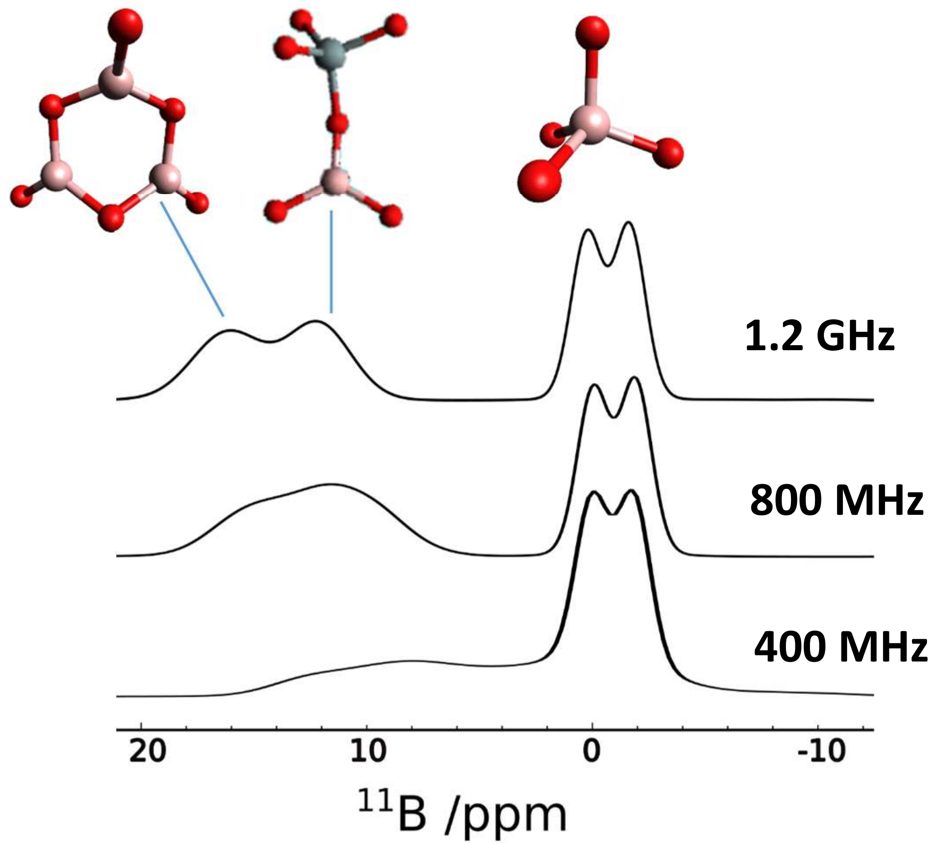
Funded by

1.2 GHz NMR will provide new insights into the atomic-level structure of materials

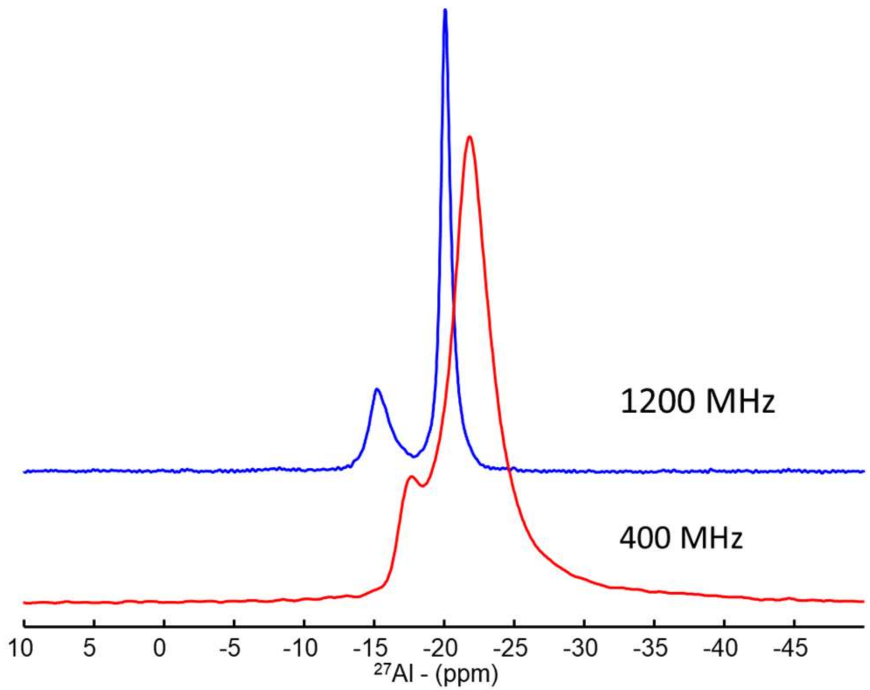
Simulated NMR spectra of ^{17}O sites



Simulated ^{11}B NMR spectra of pyrex



Solid-State High-Field NMR involved in industrial research partnerships

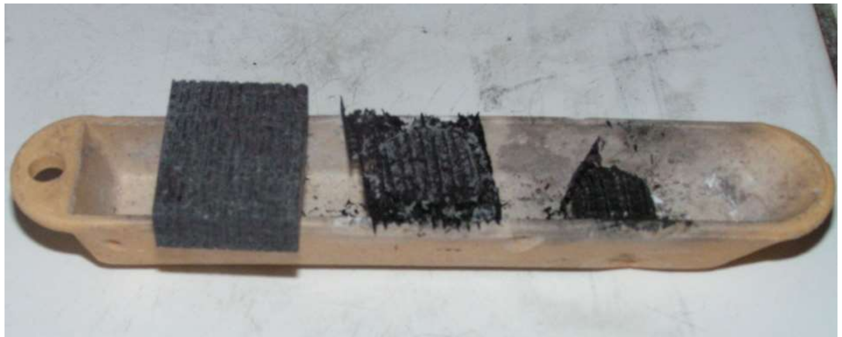


^{27}Al NMR of an anti-oxidation coating for carbon-carbon composites

SAFRAN

Smart chemistry approach to innovative antioxydation solution for aircraft carbon braking system: NMR as a optimization tool of industrial process

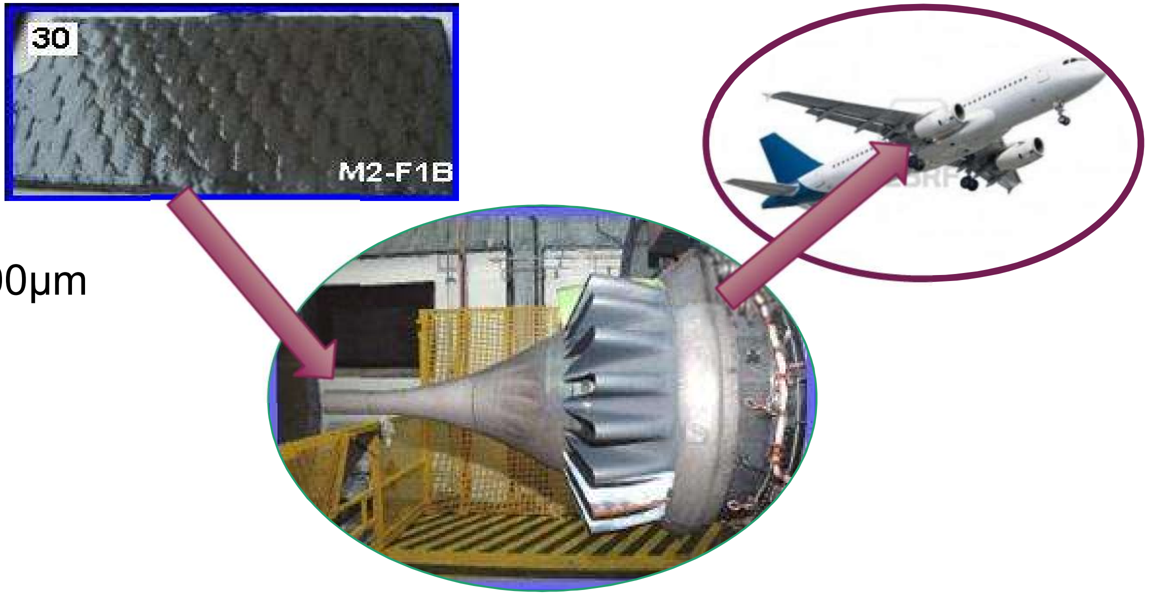
Lighter braking system means less energy consumption, but need for oxidation protection



Solid-state NMR analysis of phosphate glasses deposited as thin films

Hiroki Nagashima, Alison Mclellan, Olivier Lafon, François Méar, Frédérique Pourpoint, Lionel Montagne*

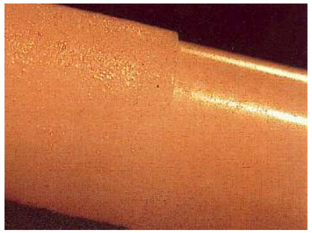
Phosphate glasses : from coatings to thin films

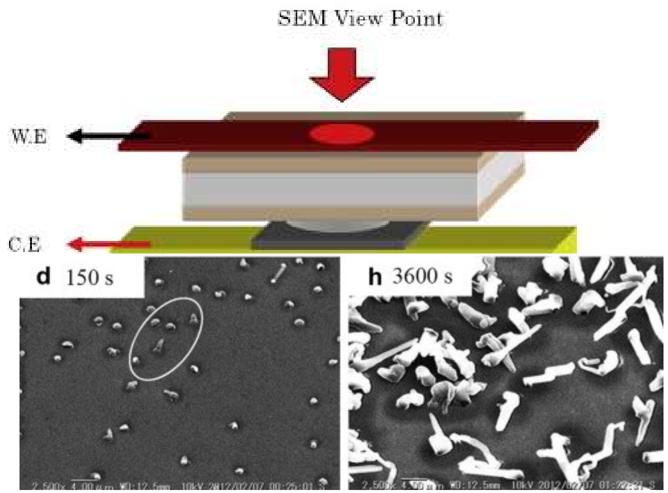


- Coatings: thickness >100µm
  - Protective enamels

for aeronautic applications

- Films 1µm< t <100µm
  - biocompatible films
  - Solid electrolytes for Li batteries

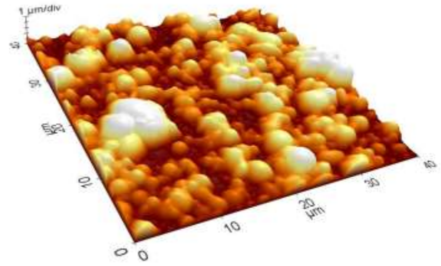




F. sagane, J. Power S. (2013)

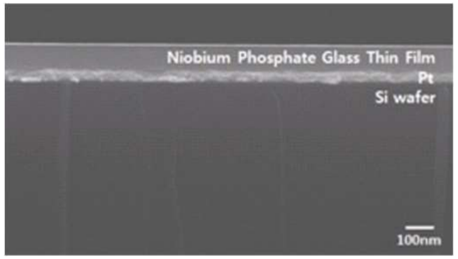
Phosphate glasses : from coatings to thin films

- Thin films : thickness <µm
  - quantum confinement phenomena in optoelectronics and optics (CdSe doped LAP glass, 60nm)



(wt. %): 70 P_2O_5 -8 Al_2O_3 - 19 Li_2O- 3 CdSe
I. Feraru, Chalc. Lett (2013)

  - Niobium Phosphate Glass Thin Film as Intermediate-Temperature Proton Conductor (100 nm)



D. Kim, Kor. J. of Mater. Res. (2018)

  - Proton-conducting zirconium phosphate glass thin films (spin deposition of sol-gel, 100-200 nm)

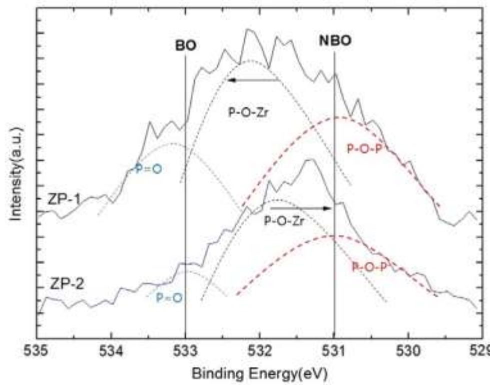
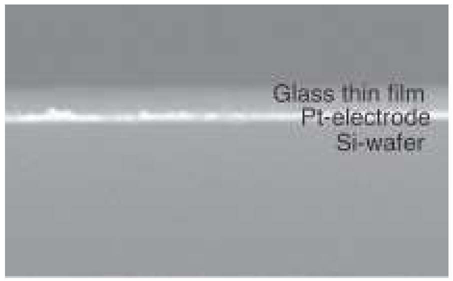


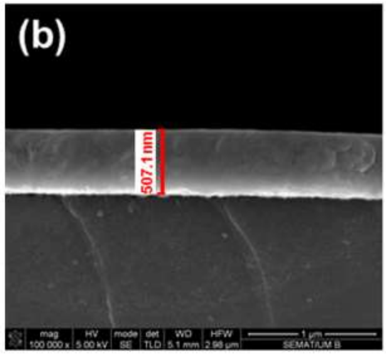
Fig. 4. XPS O_{1s} spectrum of the zirconium phosphate glass thin films.

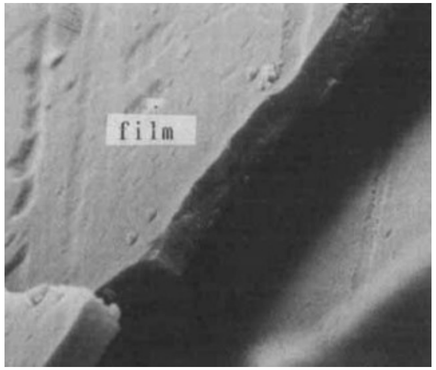


Jong-Eon Kim, Solid State Ionics (2012)

Other phosphate films, crystalline

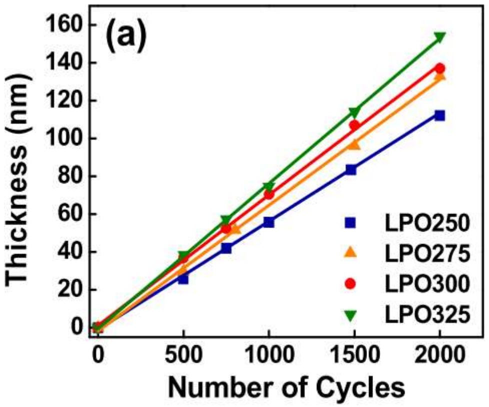
- Atomic layer deposition of lithium phosphates as solid-state electrolytes for all-solid-state microbatteries, 500 nm, *Wang, Nanotechnology 25 (2014)*

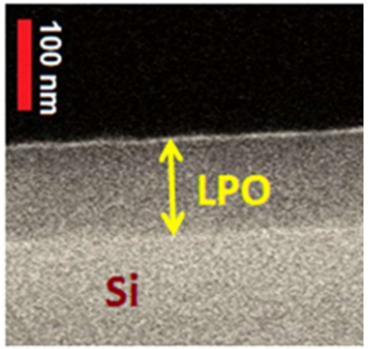


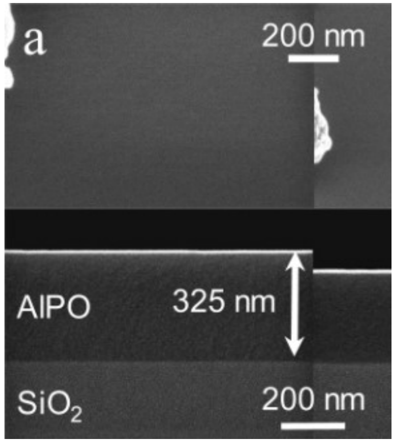


- Apatite thin-films by RF sputtering of Ca-phosphate glasses *Yamashita, J. Am. Ceram. Soc (1994)*

- Electrical insulation properties of RF-sputtered LiPON layers towards electrochemical stability of lithium batteries, *Vieira, J. Phys. D: Appl. Phys. 49 (2016)*





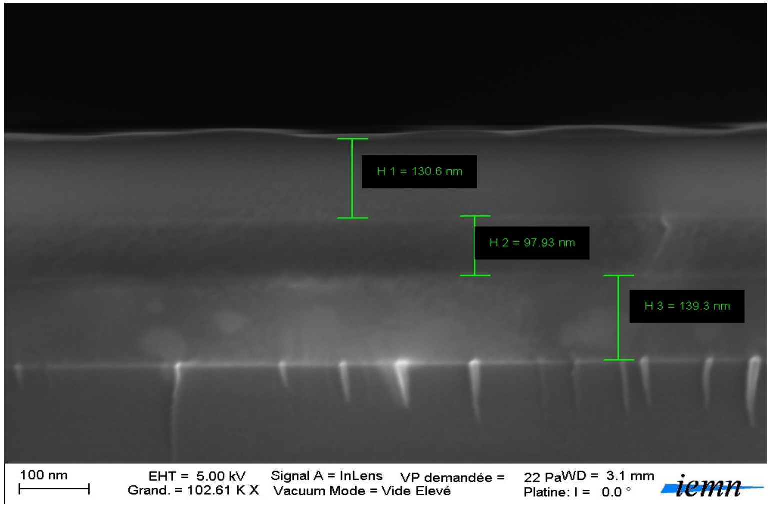


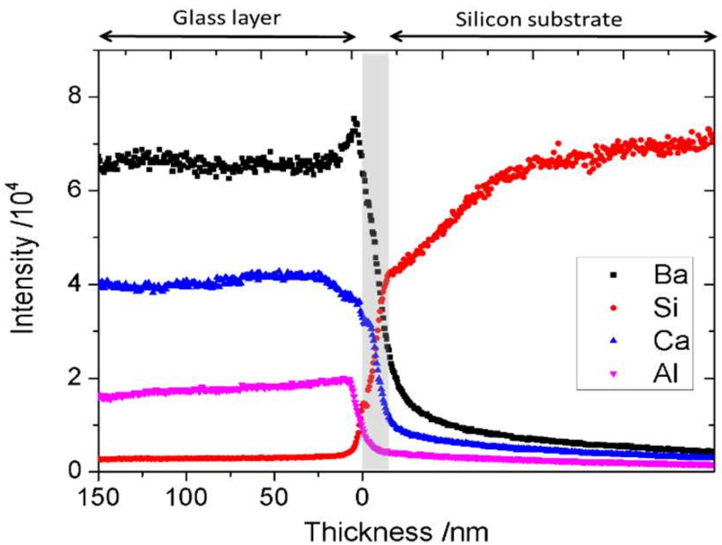
Solution-Processed Aluminum Oxide Phosphate Thin-Film dielectrics, *Meyers, Chem. Mater. (2007)*

Morphologic and compositional analysis of thin films

- Microstructure :
  - SEM, TEM
  - AFM
- Composition :
  - XPS
  - Tof-SIMS

130 nm
100 nm
130 nm

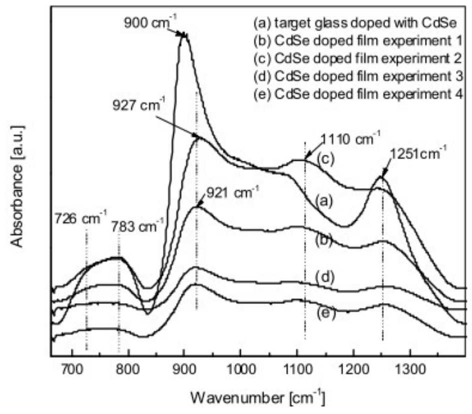




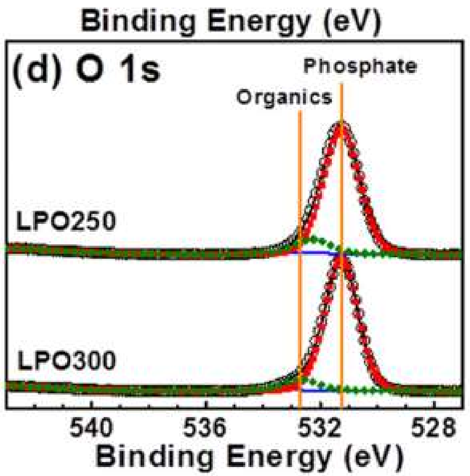
T. Carlier, Appl. Surf. Sc. (2017)

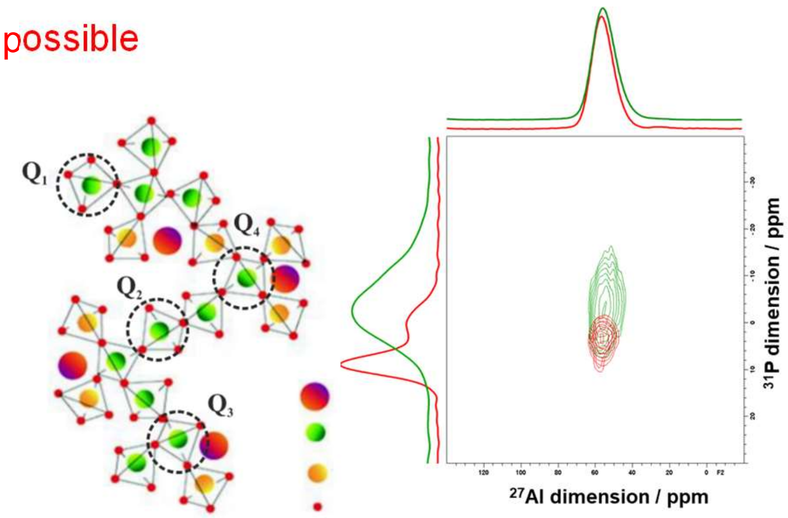
Investigation of network structure of glassy thin films

- XPS
  - Surface sensitive, direct measurement on surface
  - Indirect information on network structure
- FT-IR / Raman
  - Highly sensitive, direct measurement on surface
  - Difficult to assign for complex compositions
- NMR
  - Informative for complex networks
  - Low sensitivity, no direct measurement possible



I. Feraru, Chalc. Lett (2013)





B. Wang, Nanotechnology 25 (2014)

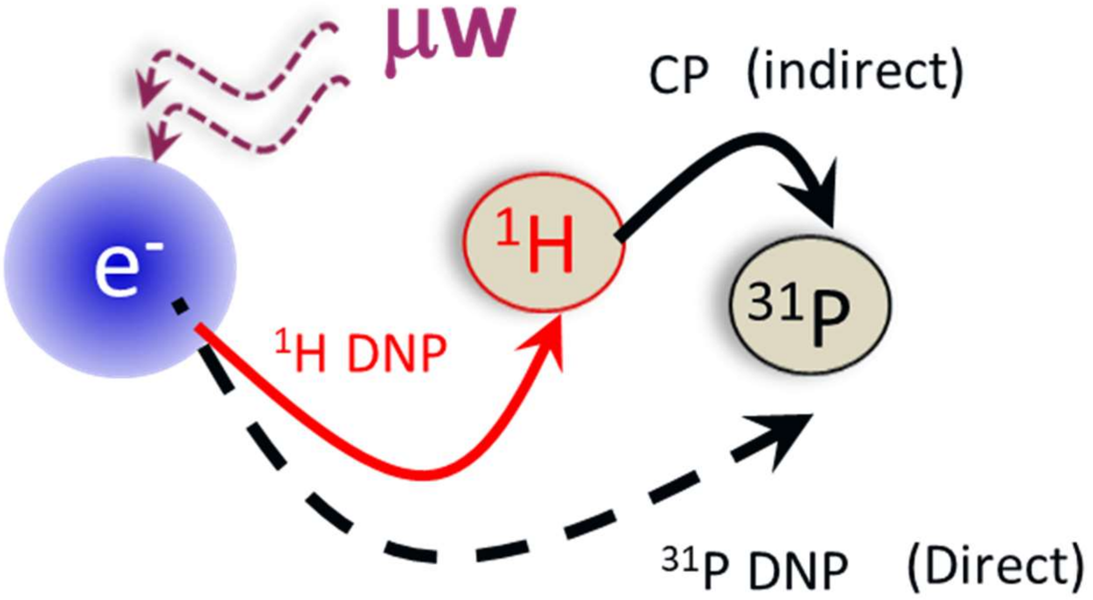
Increasing NMR sensitivity

- ^{31}P is a highly sensitive nucleus (100% natural abundance, large Larmor frequency). But somewhat large T1 relaxation time and chemical shift anisotropy.

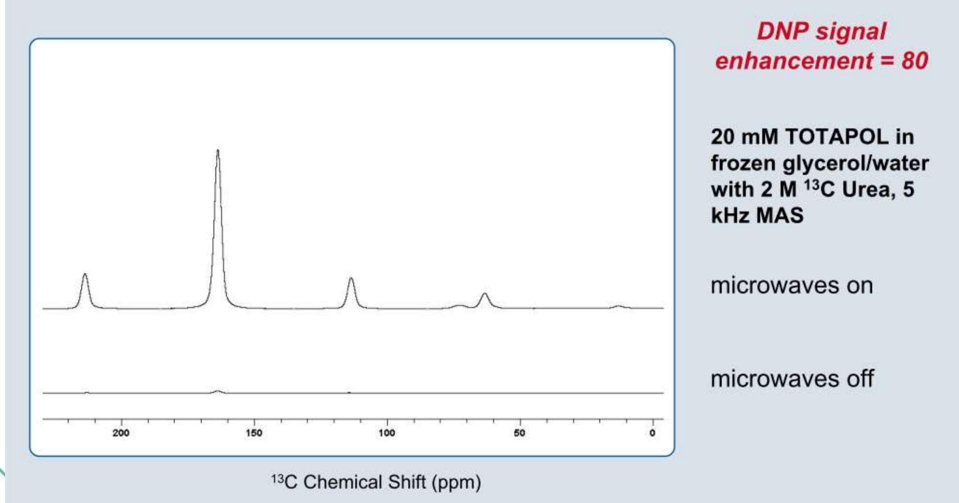
- Increasing of NMR sensitivity is possible through :
  - High field NMR (increase of sample magnetization)
  - Micro-coils (increase of RF excitation efficiency)
  - Doping with paramagnetic ions (decrease of acquisition time)
  - Dynamic Nuclear Polarization (increase of nucleus magnetization)

- Other methods are available, but they do not enable network characterization under high-resolution MAS conditions

DNP – MAS-NMR



Electron magnetization
is transferred to target nuclei

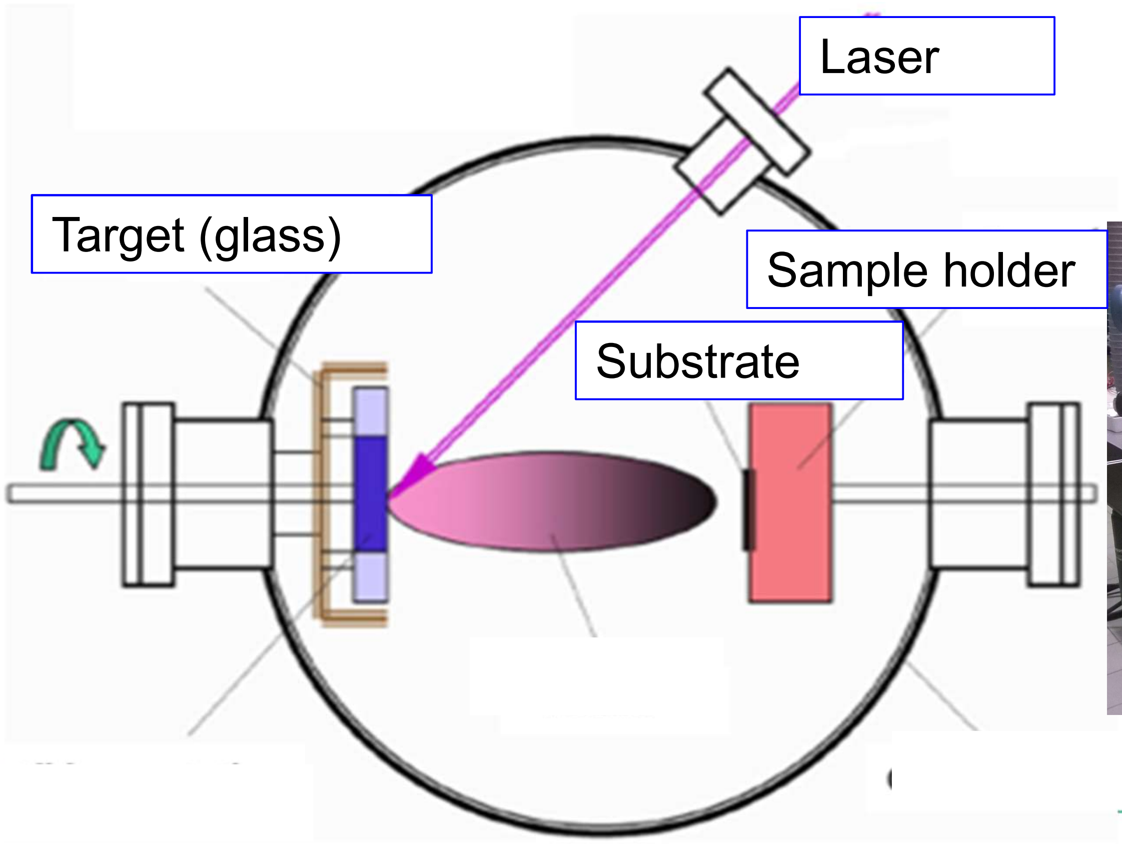


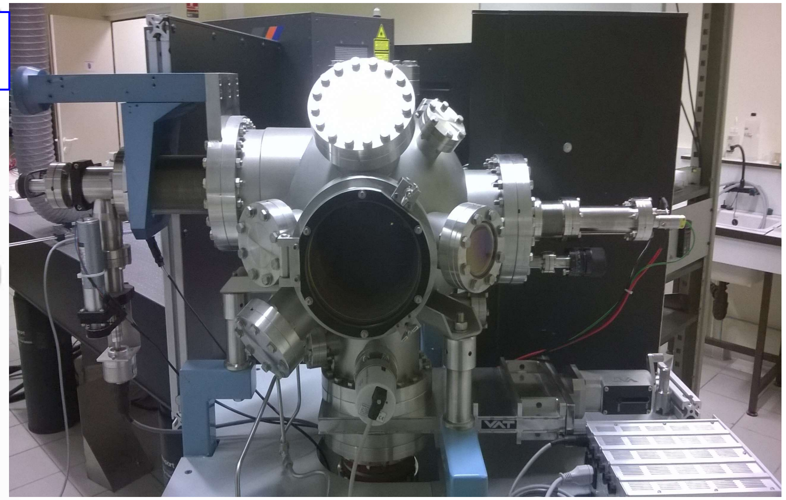
Elaboration of phosphate thin films : Pulsed Laser Deposition

$Na_5B_2P_3O_{13}$

$Pb(PO_3)_2$

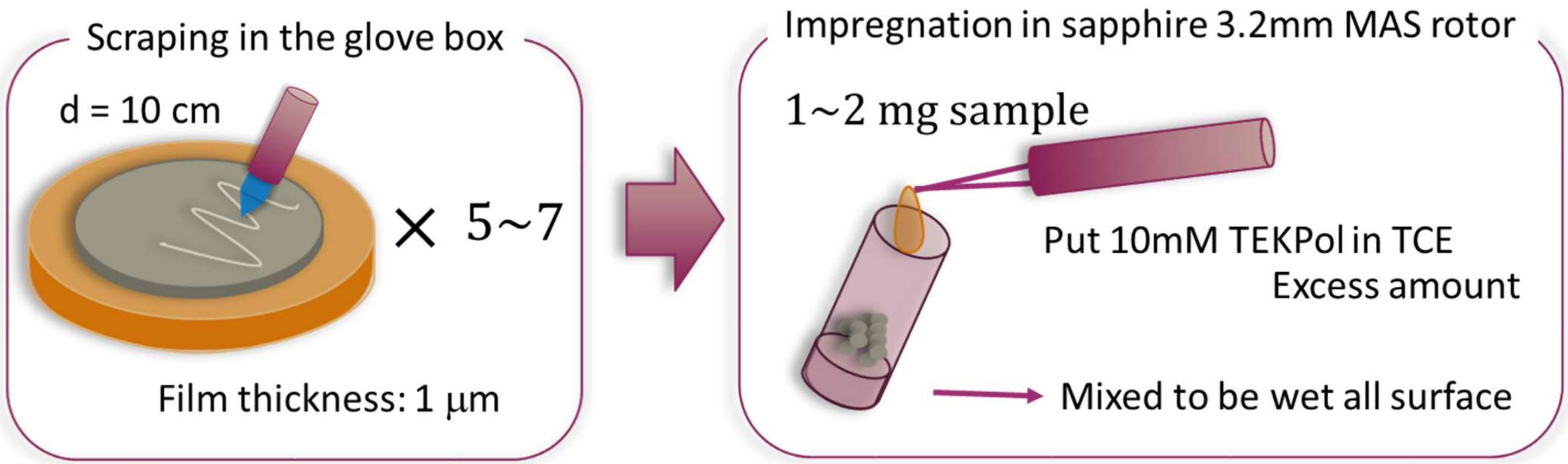
LiPON





Preparation of DNP sample

❑ Preparation



Small quantity of sample !

Considering 100 nm thickness, 5x5 cm^2 sample => Vglass= 0.3μL (1 mg)

NMR rotor volume :

0.3μL for 0.75 mm diameter, rotation speed 110 kHz (need for 5x5cm^2 sample)

6μL for 1.6 mm diameter, rotation speed 60 kHz (need for 25x25cm^2 sample)

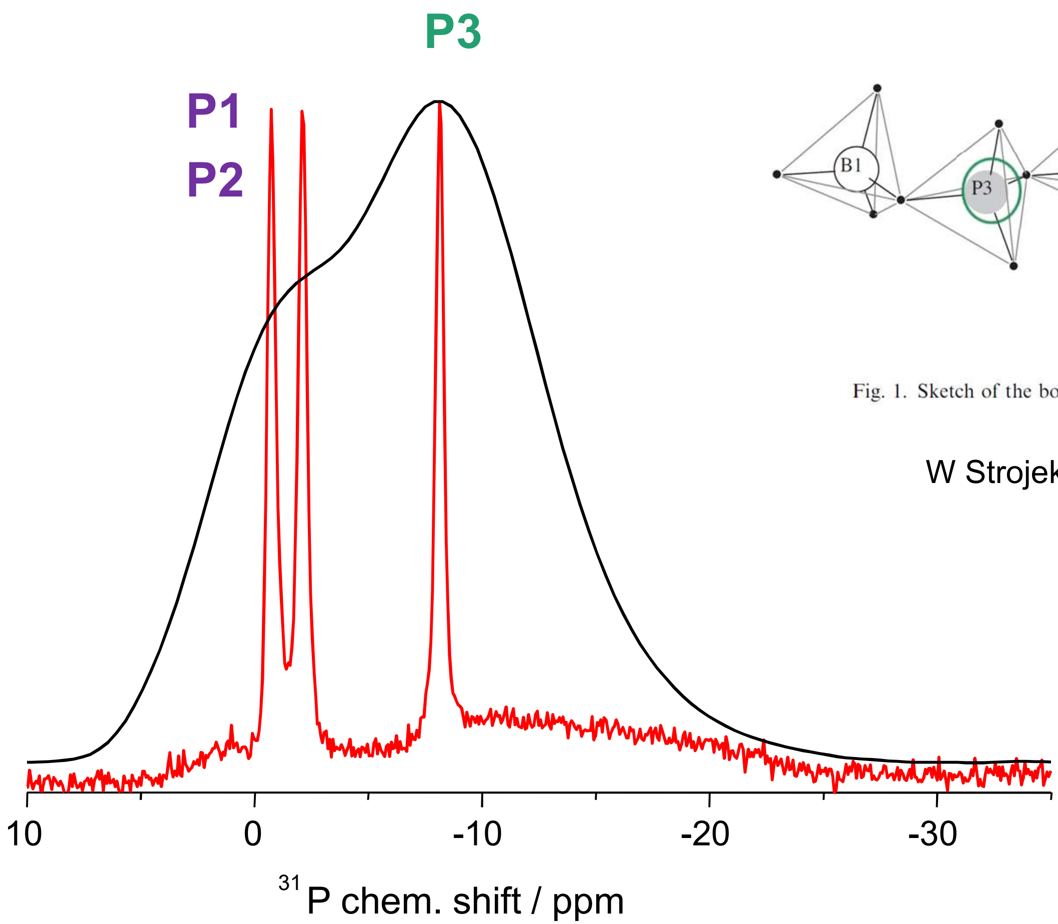
50μL for 4 mm diameter, rotation speed 15kHz (need for 70x70cm^2 sample)

=> decrease of sample volume induces a loss of signal

NMR signal-to-noise/volume ratio scales with $1/d_{coil}$ thanks to better receptivity of small coils

^{31}P MAS spectrum of bulk glass sample

$Na_5B_2P_3O_{13}$



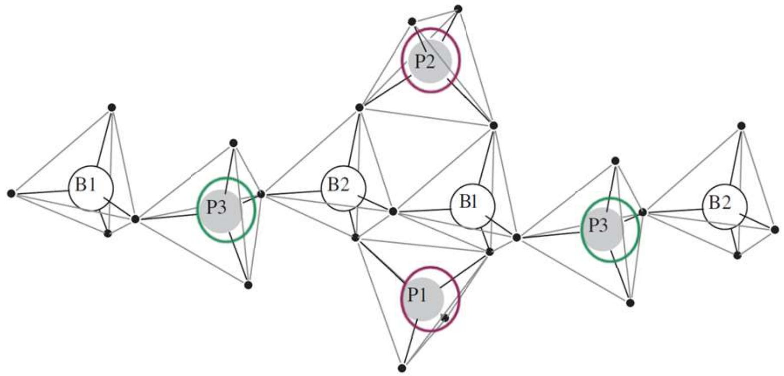


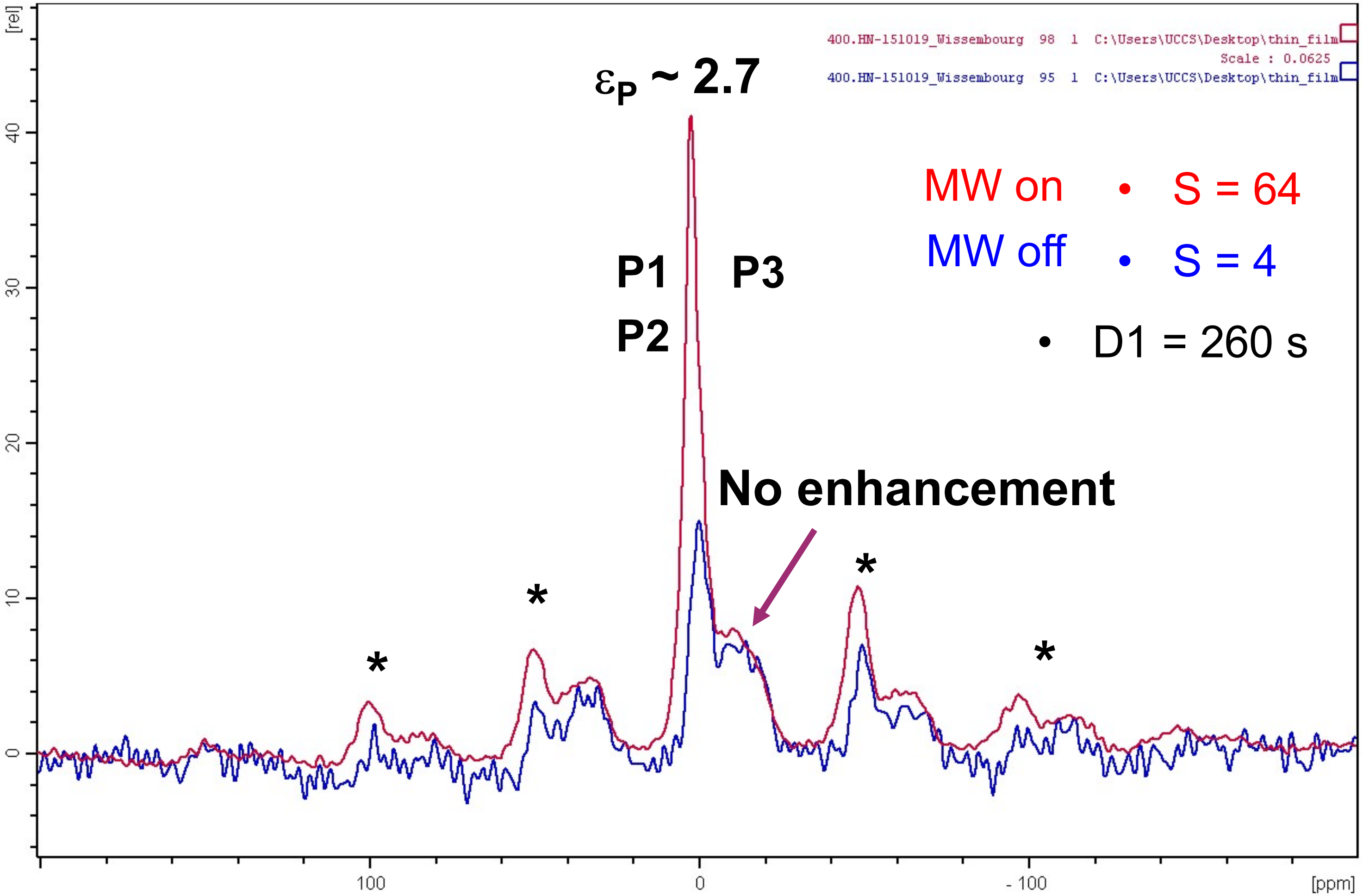
Fig. 1. Sketch of the borate–phosphate chain structure in $Na_5B_2P_3O_{13}$.

W Strojek et al SSNMR 32 (2007) 89-98

^{31}P Direct-DNP-MAS spectrum of thin glass film

$Na_5B_2P_3O_{13}$

impregnated with 15mM TEKPOL solution, MAS rate = 8kHz, T=100K, 9.4T



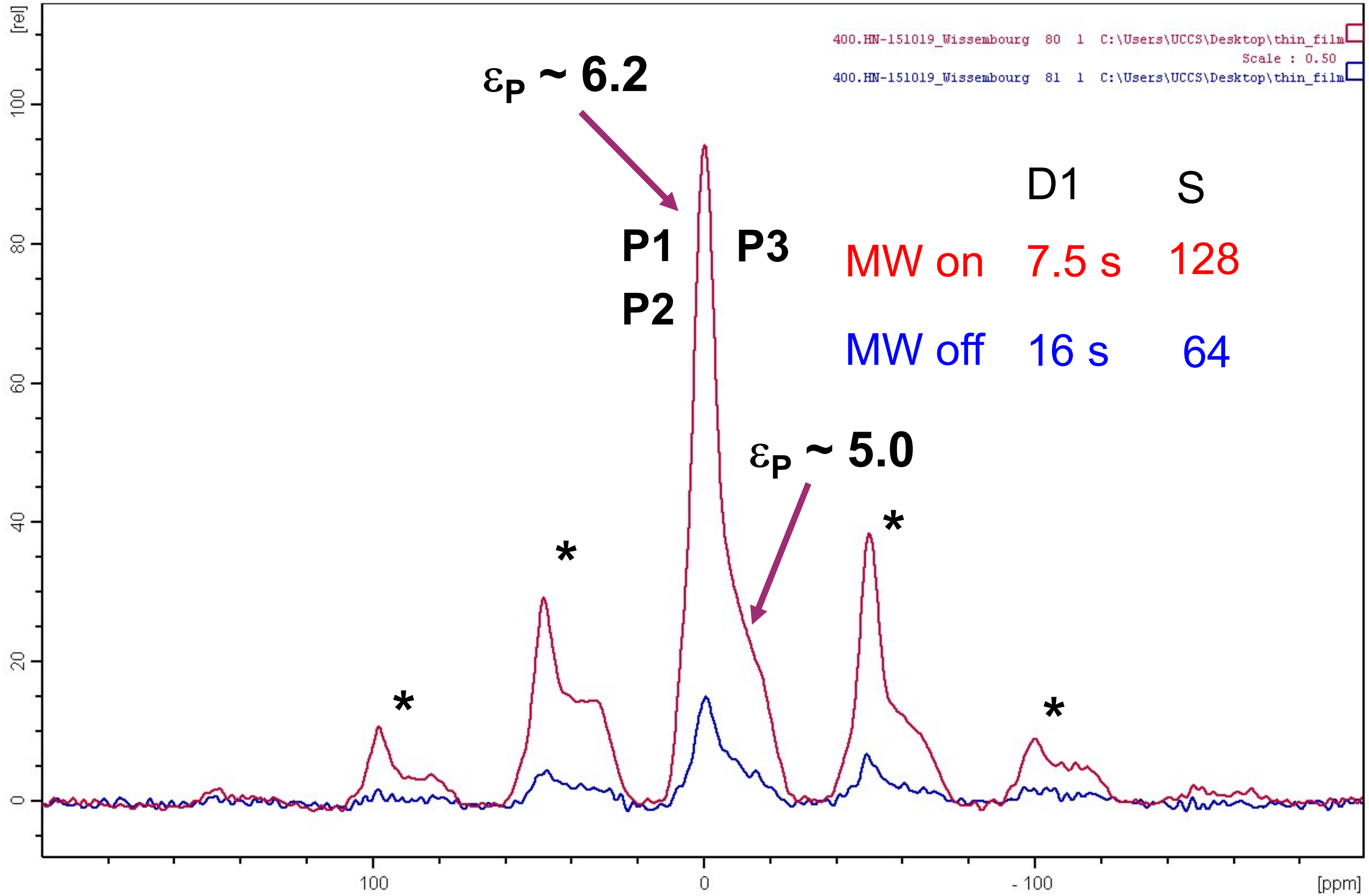
Signal enhancement is only observed on P1 and P2 sites

Spin diffusion is more efficient for P1, P2 than P3

^{31}P-{^{1}H} CP-DNP-MAS spectrum of thin glass film

$Na_5B_2P_3O_{13}$

impregnated with 15mM TEKPOL solution, MAS rate = 8kHz



Signal enhancement is observed for both P1, P2 and P3 sites

Comparison

$Na_5B_2P_3O_{13}$

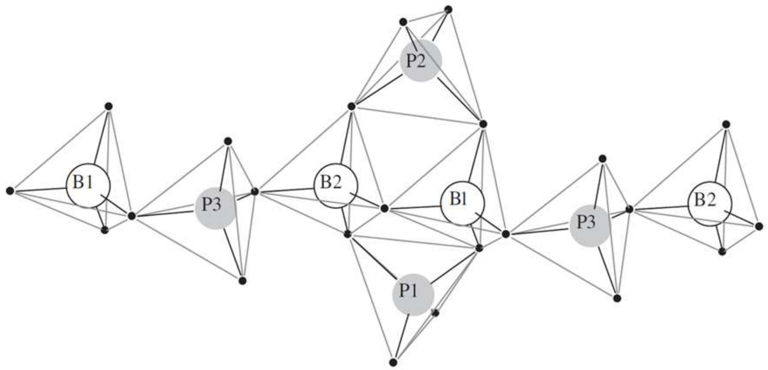


Fig. 1. Sketch of the borate–phosphate chain structure in $Na_5B_2P_3O_{13}$.

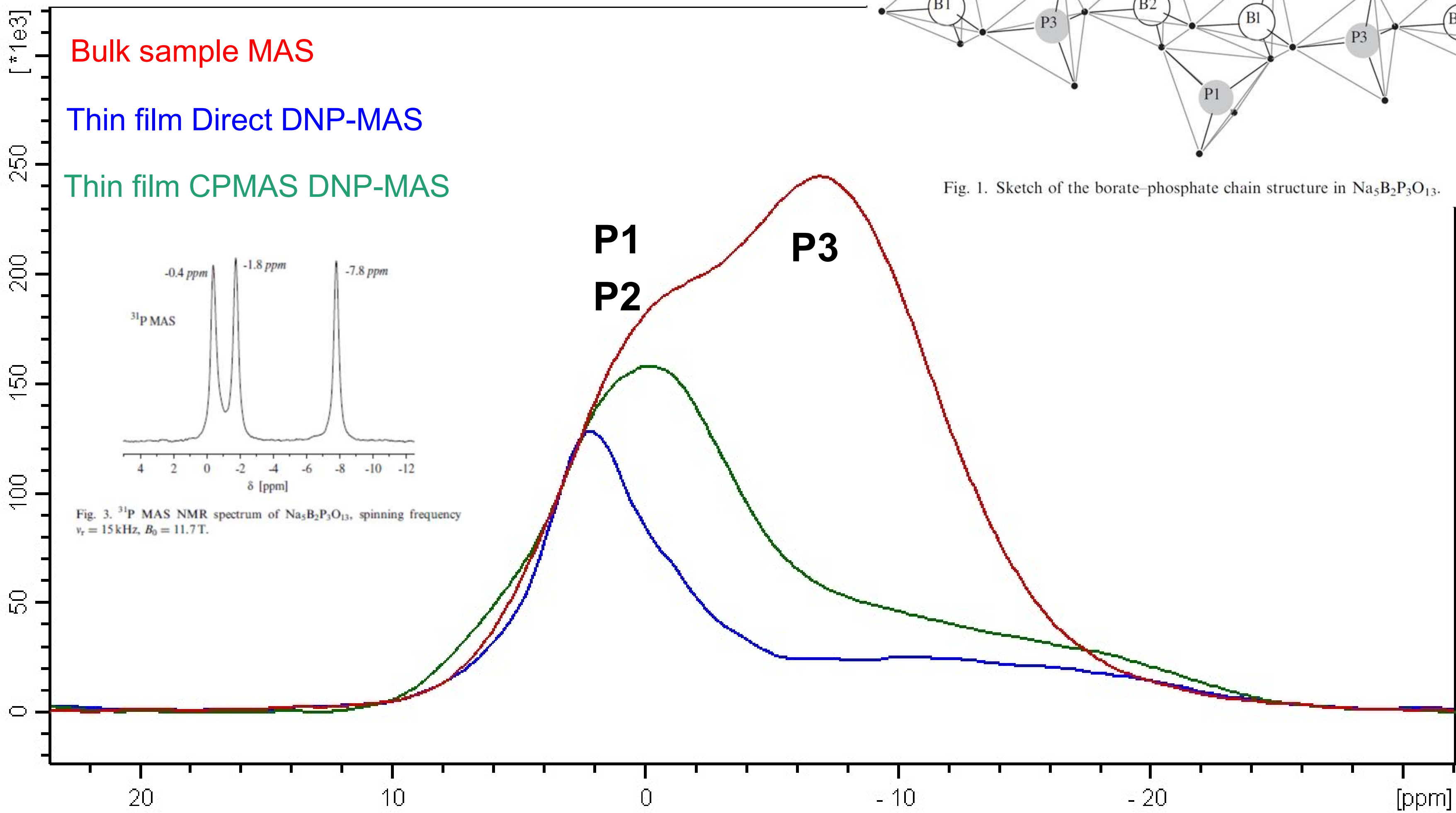
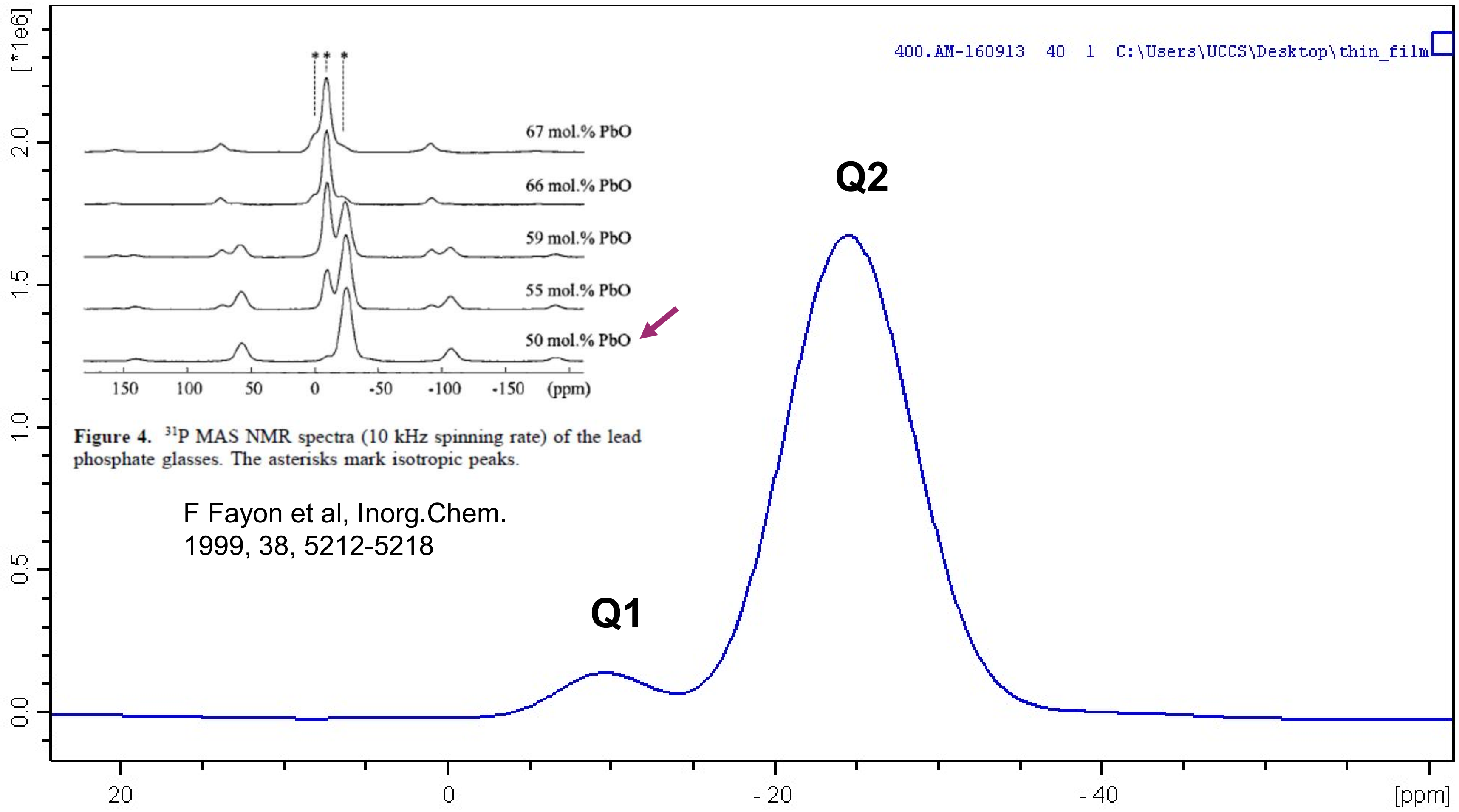


Fig. 3. ^{31}P MAS NMR spectrum of $Na_5B_2P_3O_{13}$, spinning frequency $\nu_r = 15$ kHz, $B_0 = 11.7$ T.

P1-P2 are more sensitive to DNP transfert ?
Glass thin film structure is not identical to bulk glass ?
Glass thin film structure is closer to crystal?

^{31}P Direct-DNP-MAS spectrum of bulk glass

$Pb(PO_3)_2$



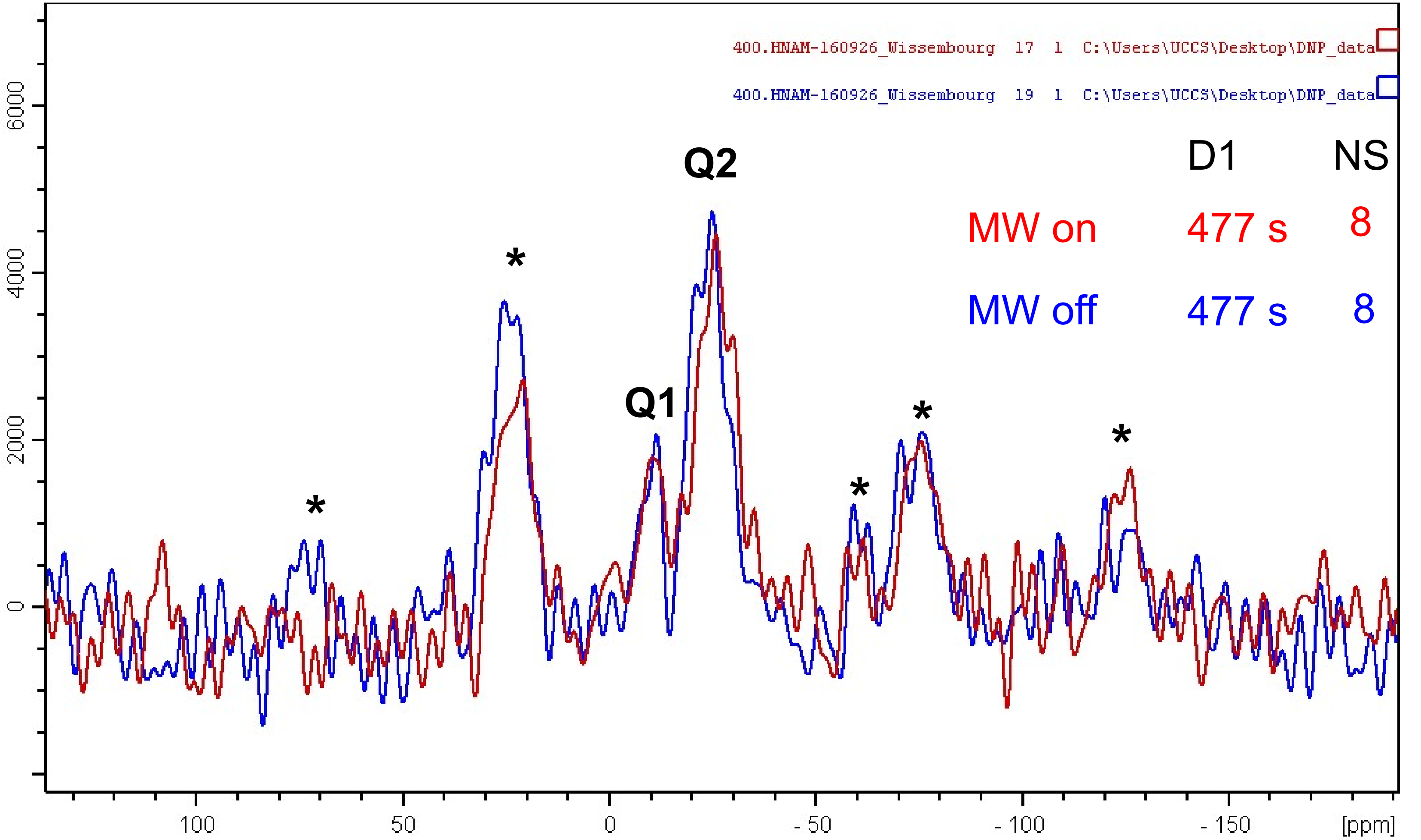
F Fayon et al, Inorg.Chem.
1999, 38, 5212-5218

UCCS

^{31}P Direct-DNP-MAS spectrum of thin glass film

$Pb(PO_3)_2$

impregnated with 15mM TEKPOL solution, MAS rate = 8kHz



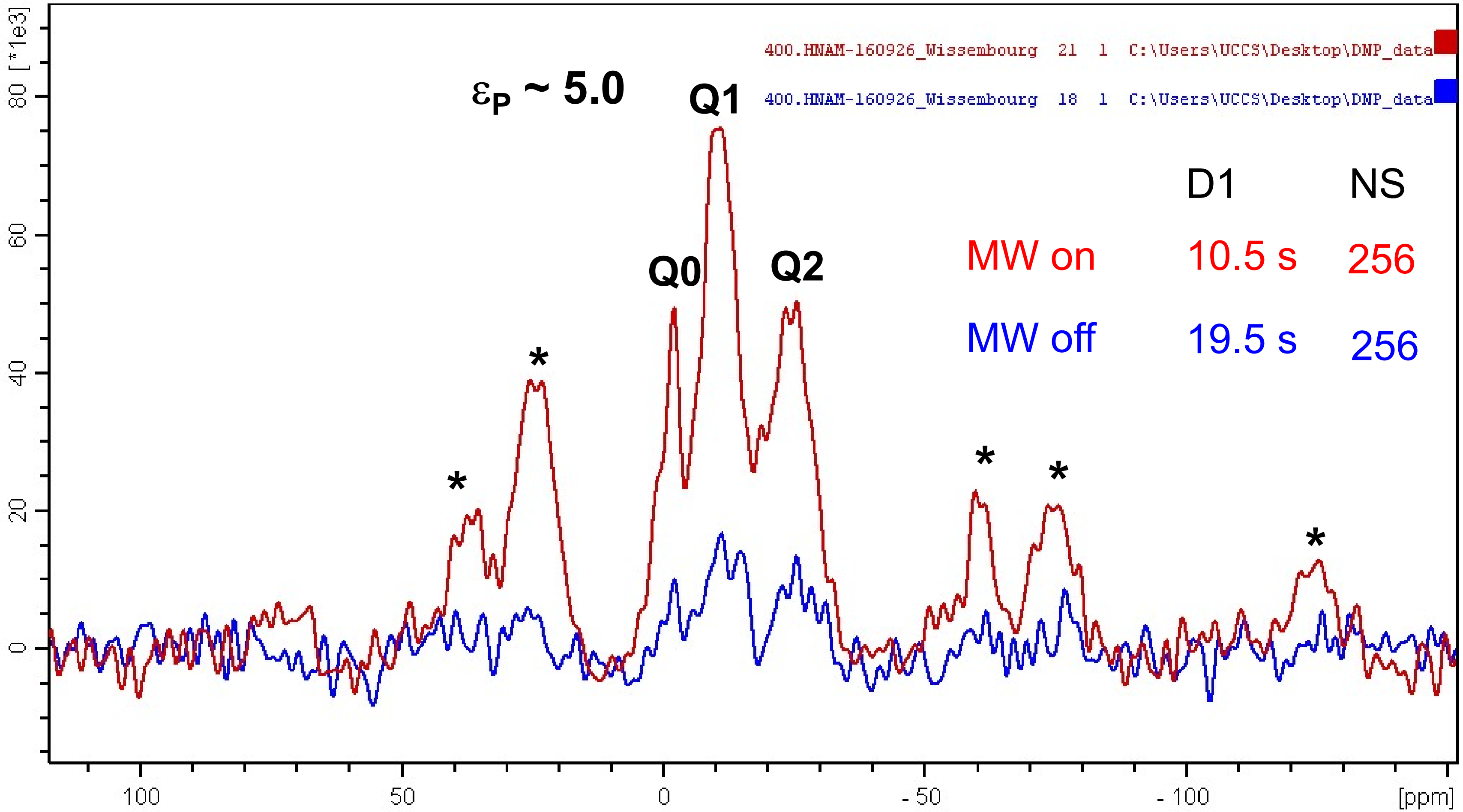
No signal enhancement through DNP is observed

Excess of Q1 : film composition is different than bulk one (shorter chains) ?

^{31}P-{^{1}H} CP-DNP-MAS spectrum of thin glass film

$Pb(PO_3)_2$

impregnated with 15mM TEKPOL solution, MAS rate = 8kHz



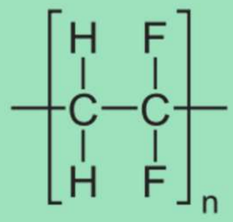
Signal is enhanced for all sites

Q^0 are observed, Q^1 intensity increases => surface signal ?

LiPON glass : Solid electrolyte in lithium ion battery
(coll. ICMC-Bordeaux)

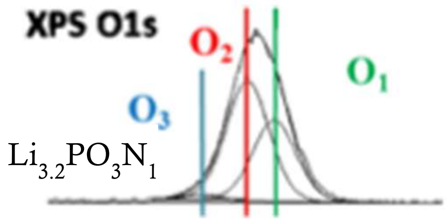
- Composition: $Li_{3.2}PO_3N_1$
- Substrate

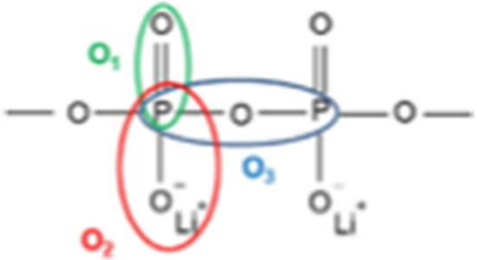
  PolyVinylidene DiFluoride (PVDF)

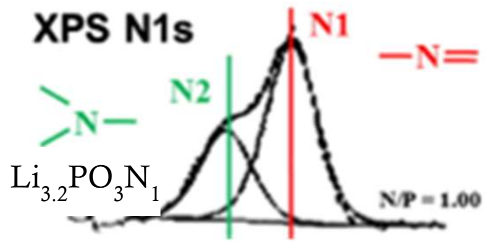


- Deposition: RF sputtering

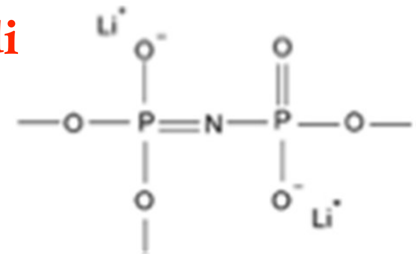
XPS



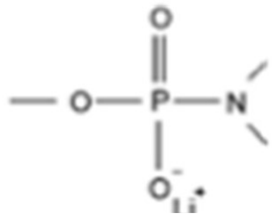




Ndi



Ntri



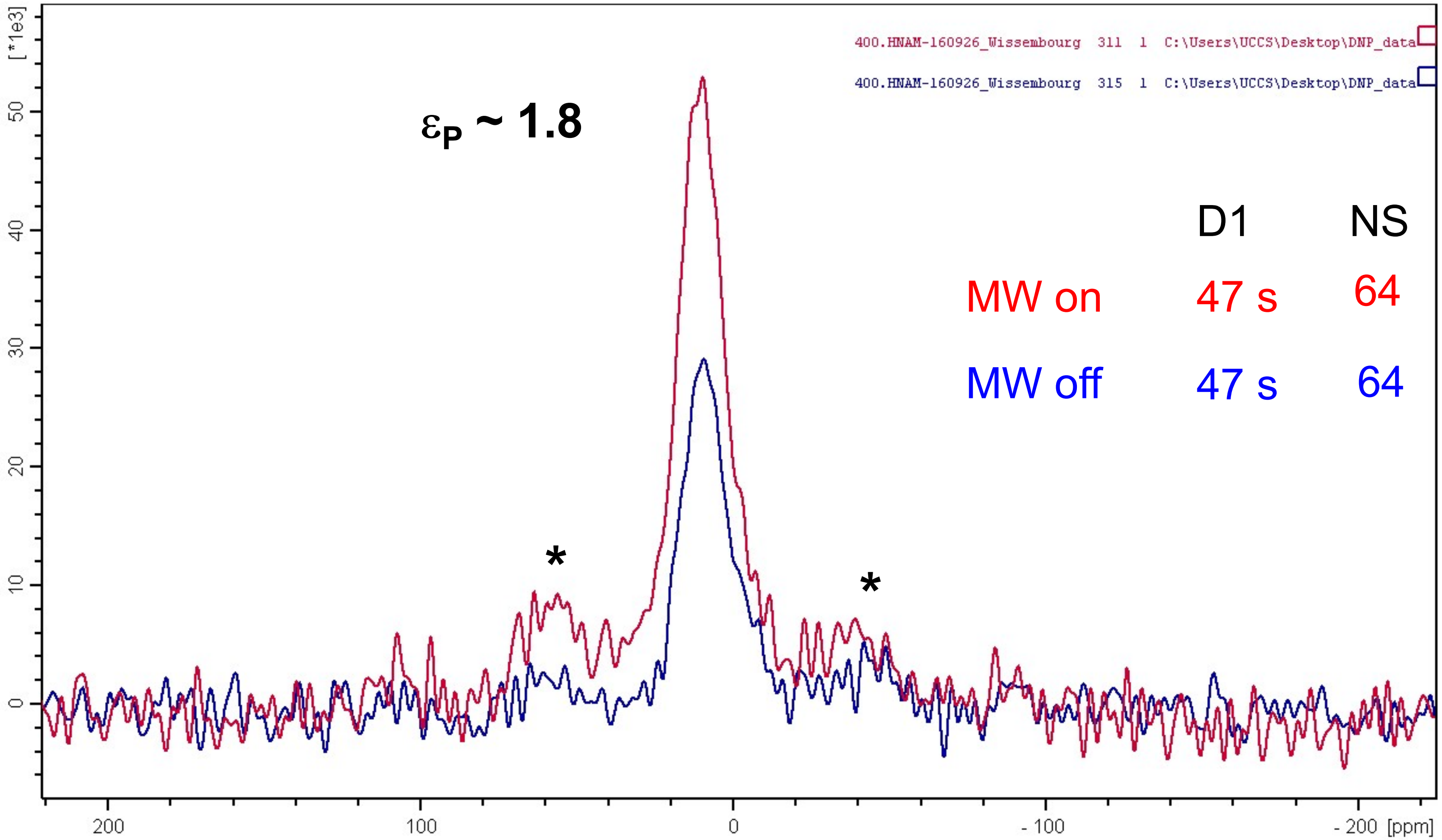
Replacement P-O-P bonds by P-N bonds

B.Fleutot et al, Solid State Ionics 186 (2011) 29-36

^{31}P Direct-DNP-MAS spectrum of thin glass film

LiPON

impregnated with 15mM TEKPOL solution, MAS rate = 8kHz

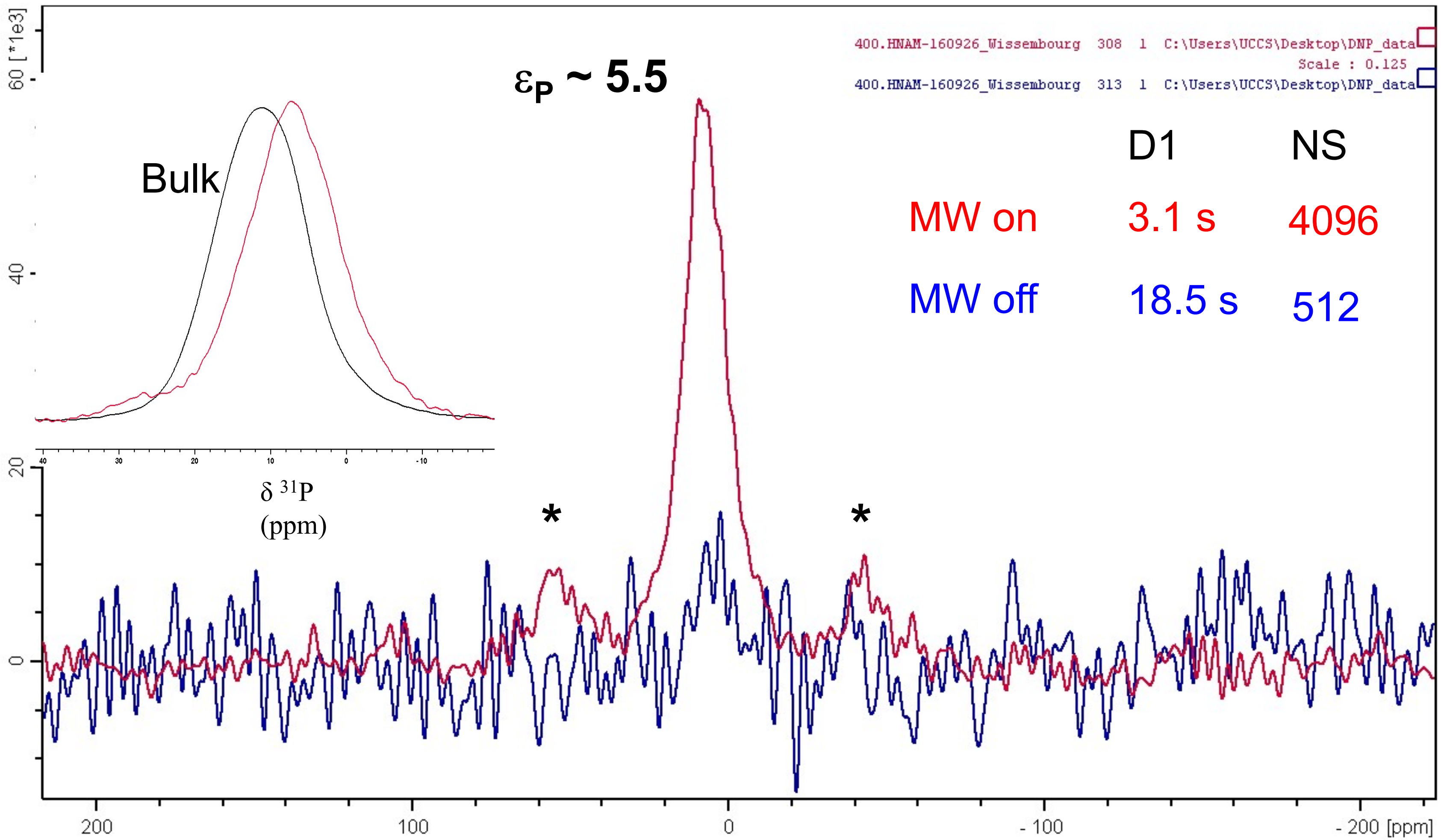


Very small signal enhancement is obained

$^{31}P-\{^{1}H\}$ CP-DNP-MAS spectrum of thin glass film

LiPON

impregnated with 15mM TEKPOL solution, MAS rate = 8kHz



Signal enhancement is obtained, (surface) film structure is different than bulk

Conclusions

- NMR analysis of thin glass layers is challenging
  - Very small sample amount
  - Difficult to scrap (and avoid alteration ?)
  - Need to control sample composition and morphology (XPS, ToF-SIMS, microscopy)
- DNP may be an efficient method to increase sensitivity
  - Need to control internal paramagnetic doping (Mn^{2+}) to enable direct DNP
  - Indirect ^{1}H-^{31}P DNP provides information on glass surface
  - Check ^{1}H doped glasses (ZrP protonic conductors)
- Deposition as thin glass layer may induce different network conformation ($Na_5B_2P_3O_{13}$ cycle/chain ratio)
- This may influence strongly thin film properties vs bulk glass (which is considered to design glass composition)

Acknowledgements

1. Florence Delahaye-carrière 1997
2. Cyrille Mercier 1996
3. Hélène Grussaute 1998
4. Sébastien Donze 1999
5. Emilie Antoni 2003
6. Julien Trebosc 2003
7. Emilie Beckaert 2004
8. Grégory Tricot 2005
9. Alexandrine Flambard 2005
10. Elodie Creton 2009
11. Filippe Vasconcelos 2010
12. Daniel Coillot 2010
13. Nina Forler 2011
14. Prashant Rajbandhari 2013
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16. Thomas Lemesle 2013
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19. Annelise Chabauty 2018
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22. Diane Sipp 2023

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MERCI à l'USTV !!

Webinaire #15: Les verres phosphate

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