Phosphate glasses,

(i) some aspects of their chemistry and related applications

(ii) Nitrided phosphate glasses : another brick in the wall ?

(i)   L. Montagne, F. Méar, L. Delevoye, University of Lille

**(ii) F. Munoz, CSIC Madrid**

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
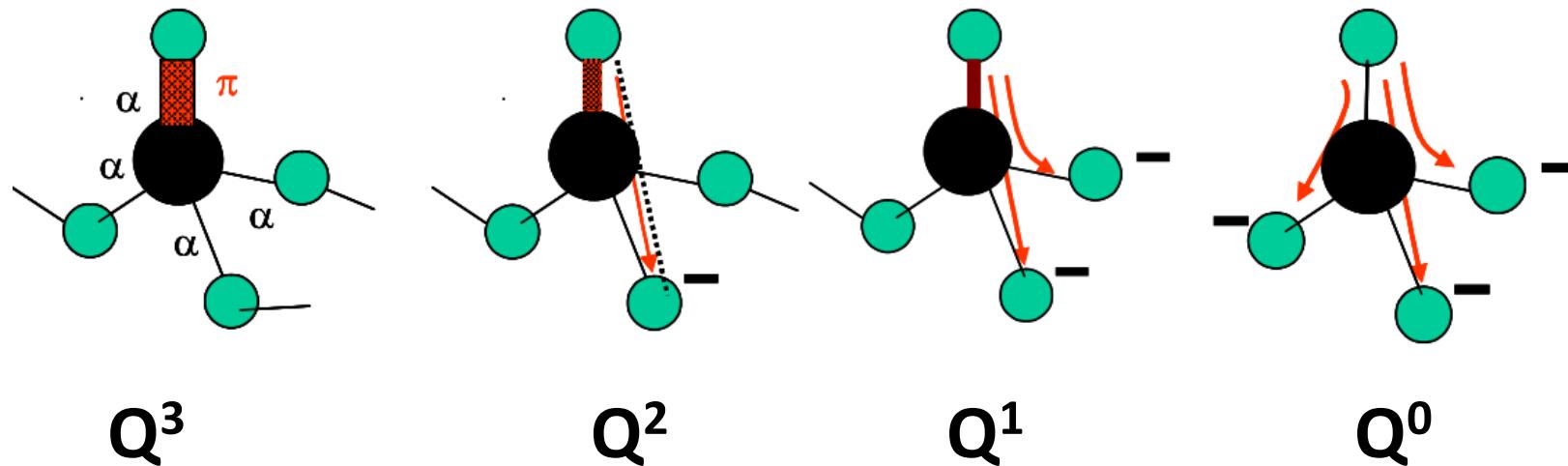
Consequence 1:

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

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

Silicate glasses

Q^4 Q^3 Q^2 Q^1 Q^0

...   .   polyphosphate   pyrophosphate   orthophosphate

P_2O_5 PO_3^- $P_2O_7^{4-}$ PO_4^{3-}

O/P   2.5   3   3.5   4

Ultraphosphates   Oligophosphates   Oxyphosphates
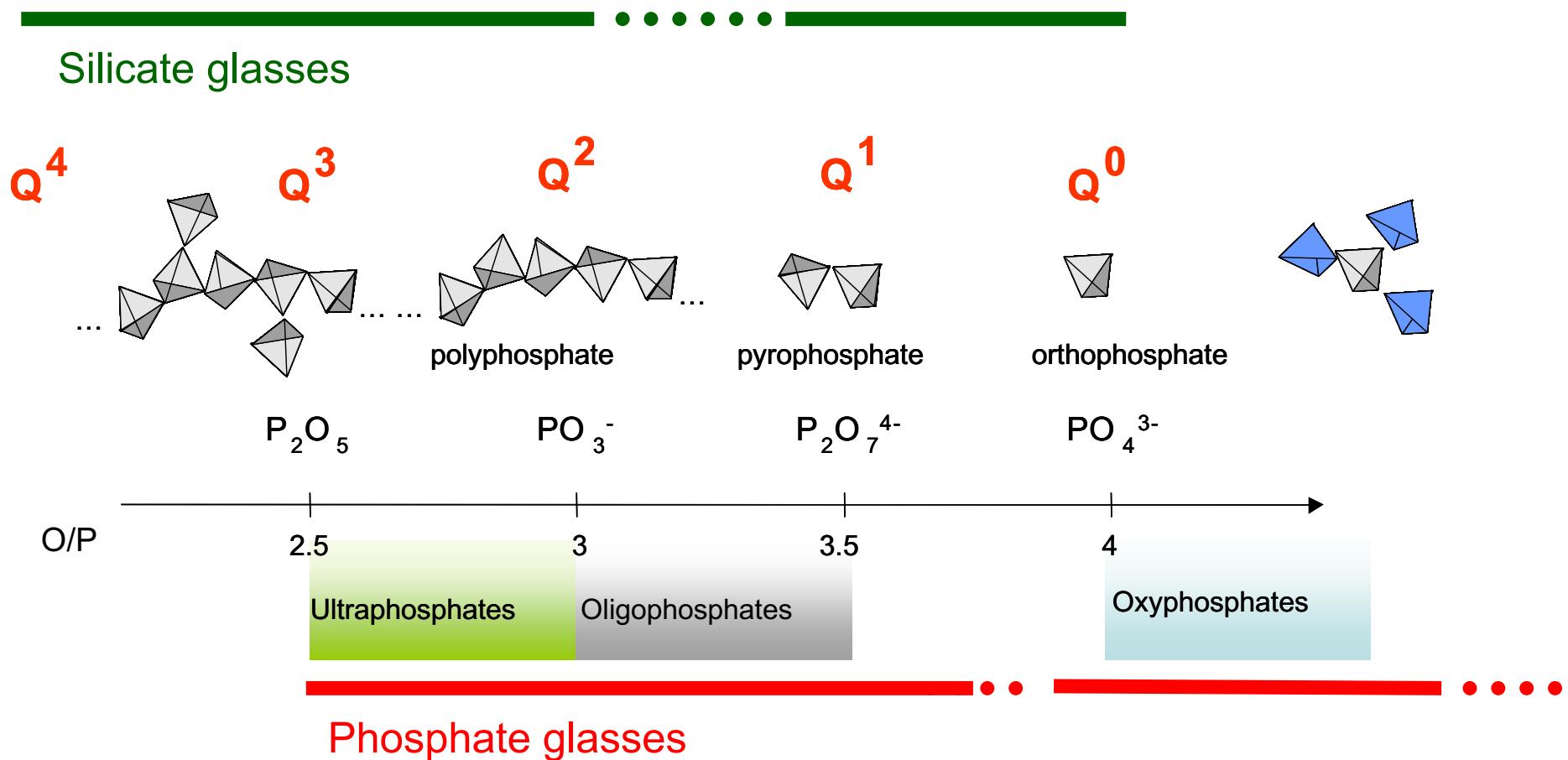
Phosphate glasses

Consequence 2:

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

    - P_2O_5 is a strong Lux & Flood acid:
        - $P_2O_5 + O^{2-} \Leftrightarrow 2PO_3^-$
    => Strong reactivity with other oxides
        - FluoX pearls
        - Mixed-network glasses…

Silicate glasses

Q^4 Q^3 Q^2 Q^1 Q^0

... ... polyphosphate ... pyrophosphate orthophosphate

P_2O_5 PO_3^- $P_2O_7^{4-}$ PO_4^{3-}

O/P

O/P

2.5 3 3.5 4

Ultraphosphates Oligophosphates Oxyphosphates

Phosphate glasses Mixed network phosphate glasses
(Alumino-, Boro-, Vanado-, …)
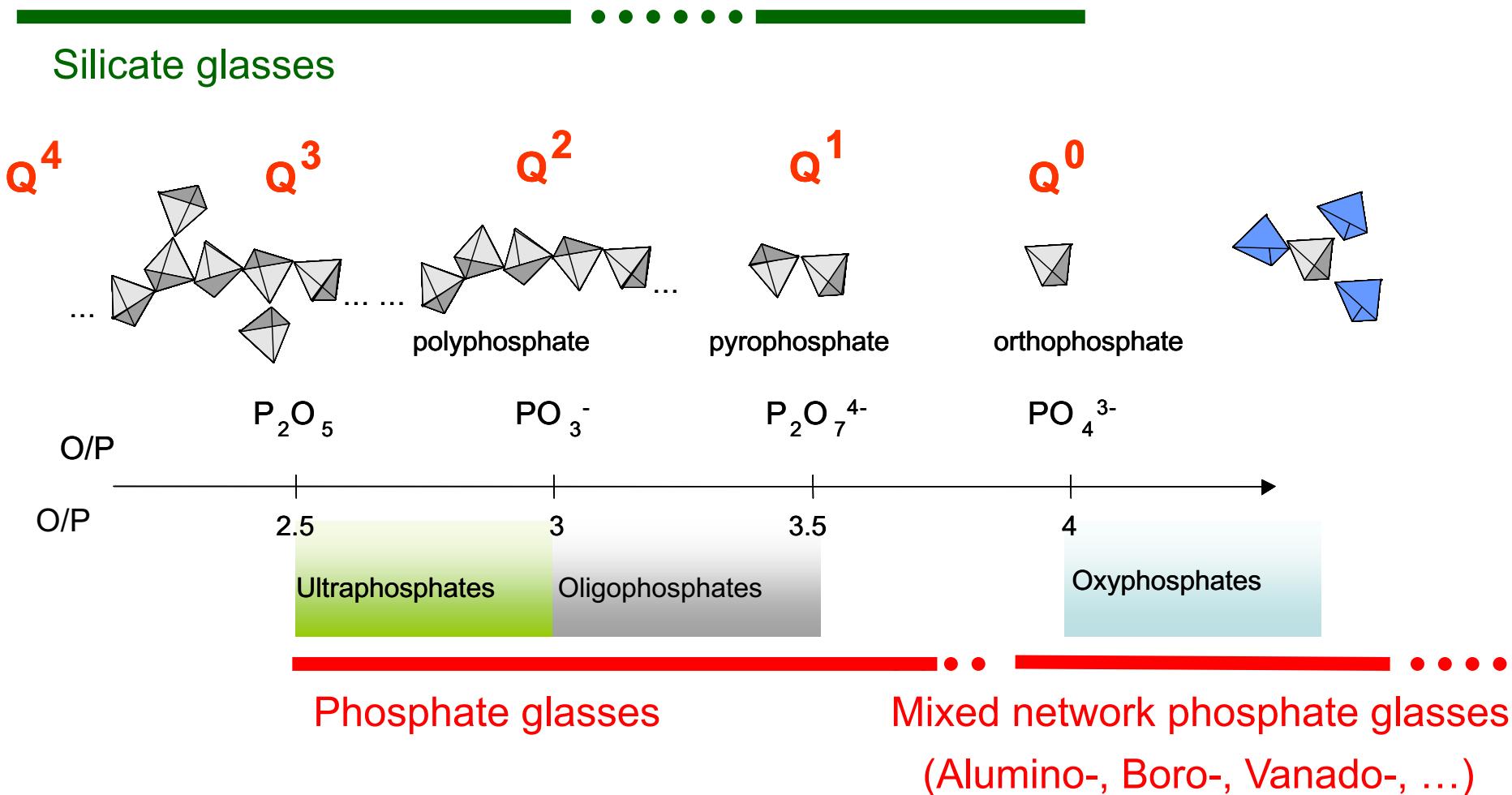
Phosphate laser glass

National Ignition Facility (US) Laser, Megajoule Laser (F)

Nd-doped Ba metaphosphate (Q^2 glasses)

- 3000 glass slabs :
  - Index uniformity to $<\pm0.000001$
  - 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

  $\Rightarrow$ High Nd content without clustering effect

Beamlet eighteen liter rare earth doped phosphate glass amplifier slab

Glasses for nuclear waste immobilization :
less polymerized network enables to incorporate large anions ?

Q2 : Metaphosphate glasses for nuclear wastes with high sulfate content

CEA – CNRS GNR MATINEX (2010)

Q2+Q1: Silver tripolyphosphate glasses for radioactive I immobilization

CEA PhD T. Lemesle (2013) A. Chabauty (2018)

BaO

BaSO$_4$
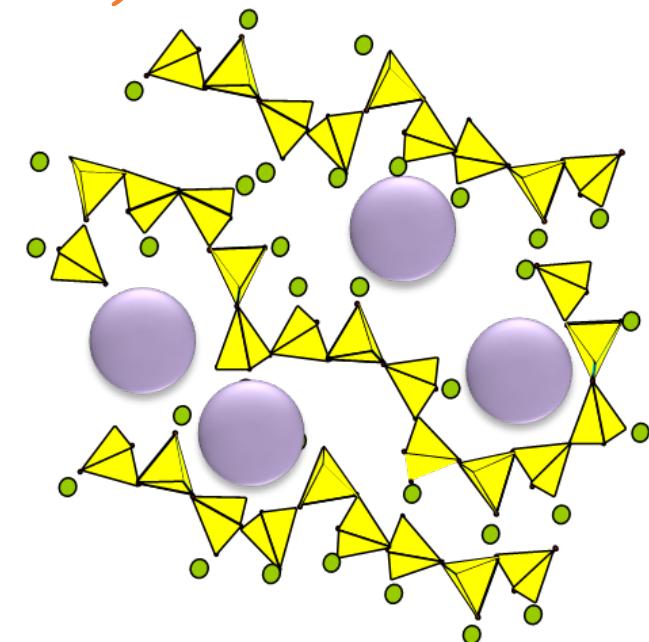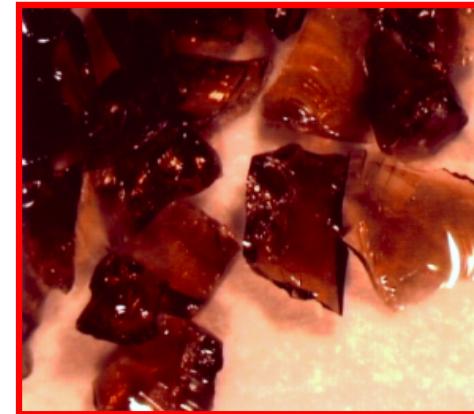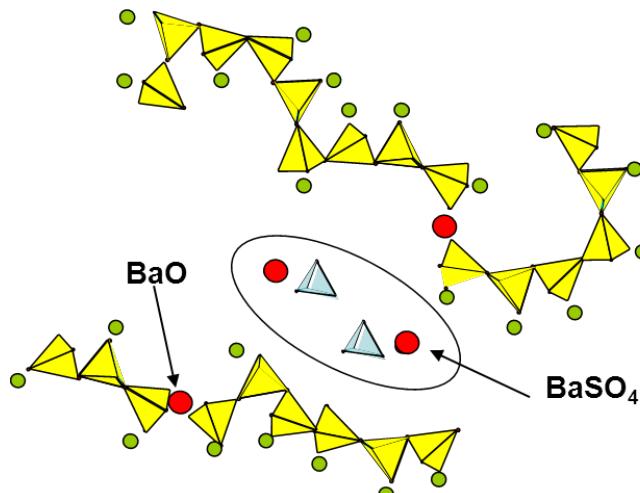
Zinc pyrophosphate glasses 66ZnO-33P_2O_5 (Q^1 network)

- Laser inscription, precipitation of silver nanoclusters.
- Why such network ? Low connectivity enables fast local reorganization ?

L. Cannioni , T. Cardinal (2010)
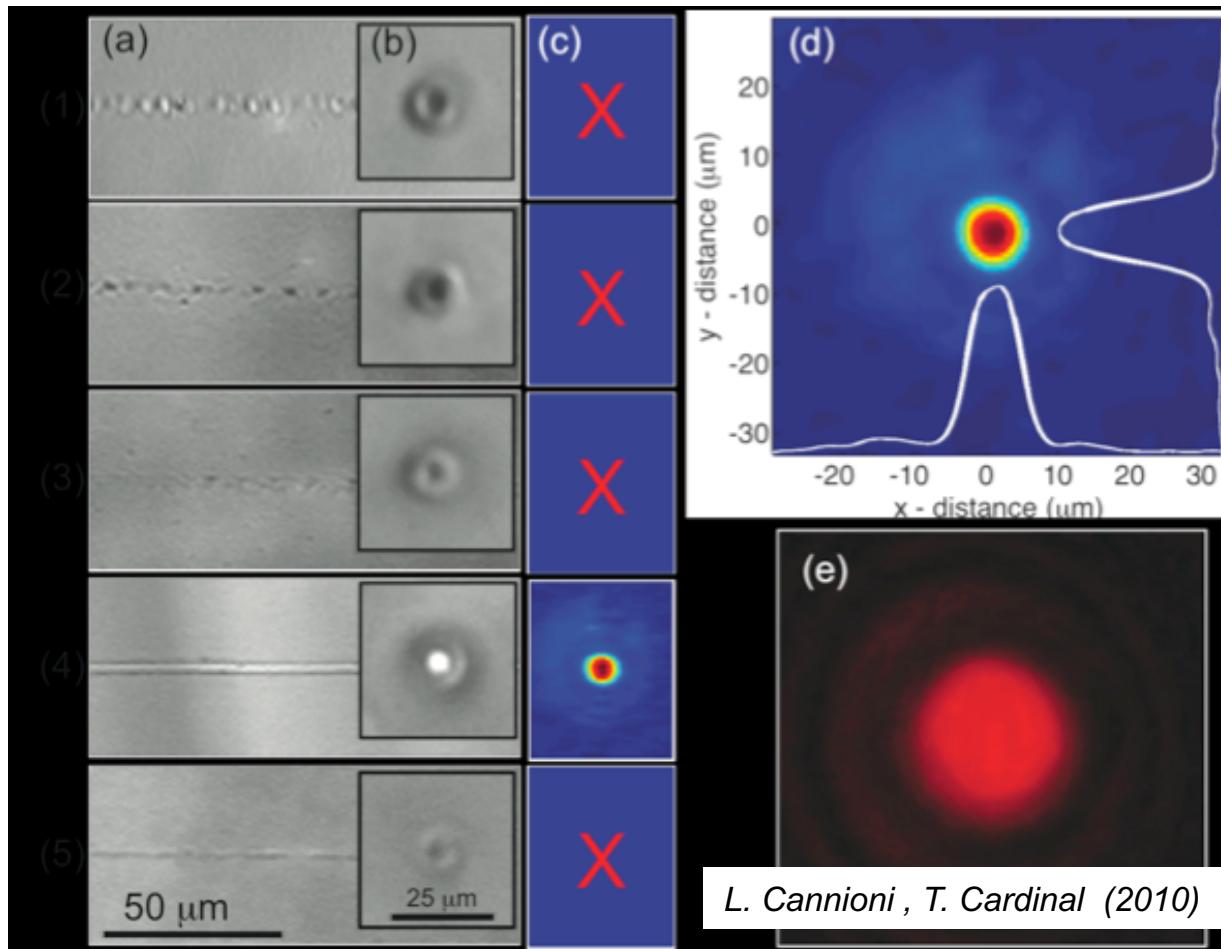
Other consequences of low network connectivity

=> 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

=> *Low chemical durability !*

Al, Cu alloys, CTE#25.10^{-6}ppm.K^{-1}
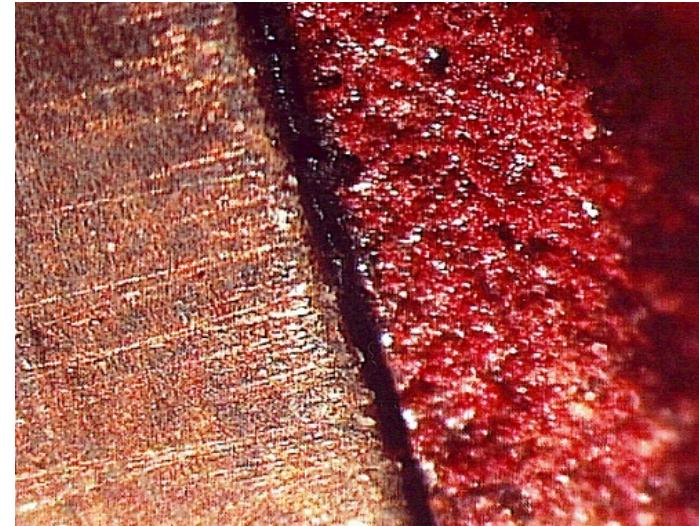
Sealing of BiMeVOx to Stainless steel (SOFC fuel cells)
CTE#$16-17.10^{-6}$ppm.K^{-1}
Bi_2O_3 highly reactive
Formulation of Bi_2O_3-V_2O_5-P_2O_5 glass

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)

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*
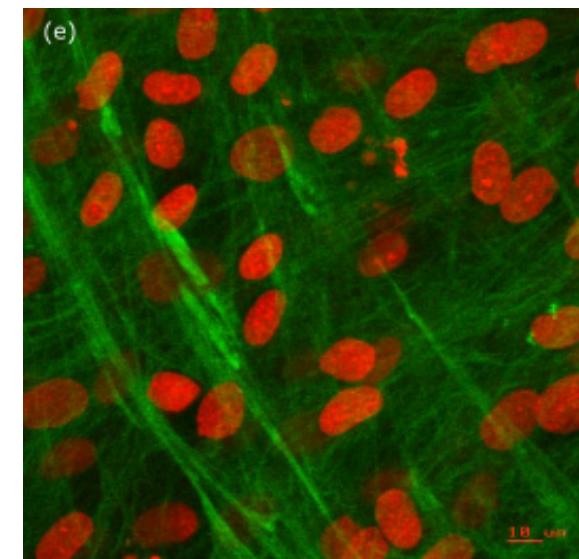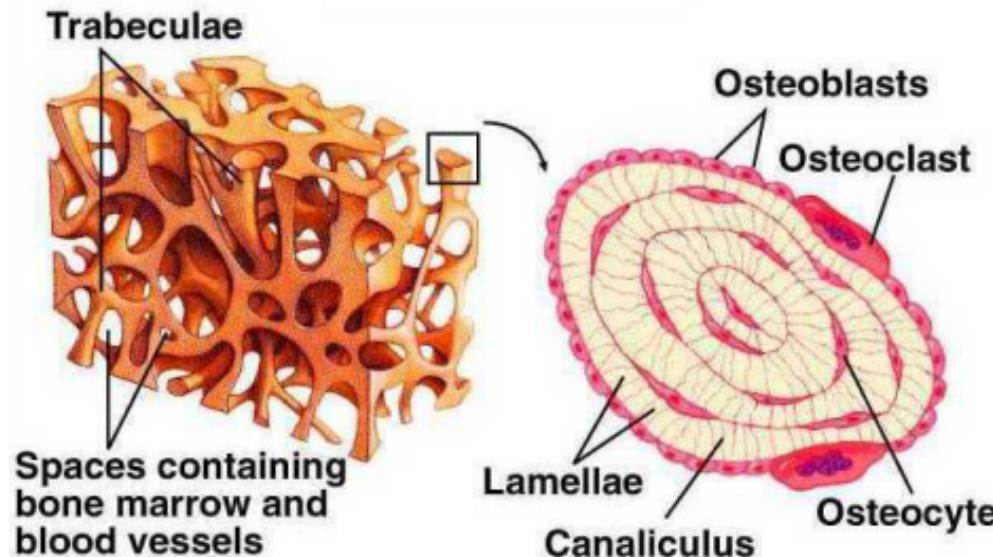
Knowles Acta Biomaterialia (2012)

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

Mixed-network phosphate glasses : aluminophosphates
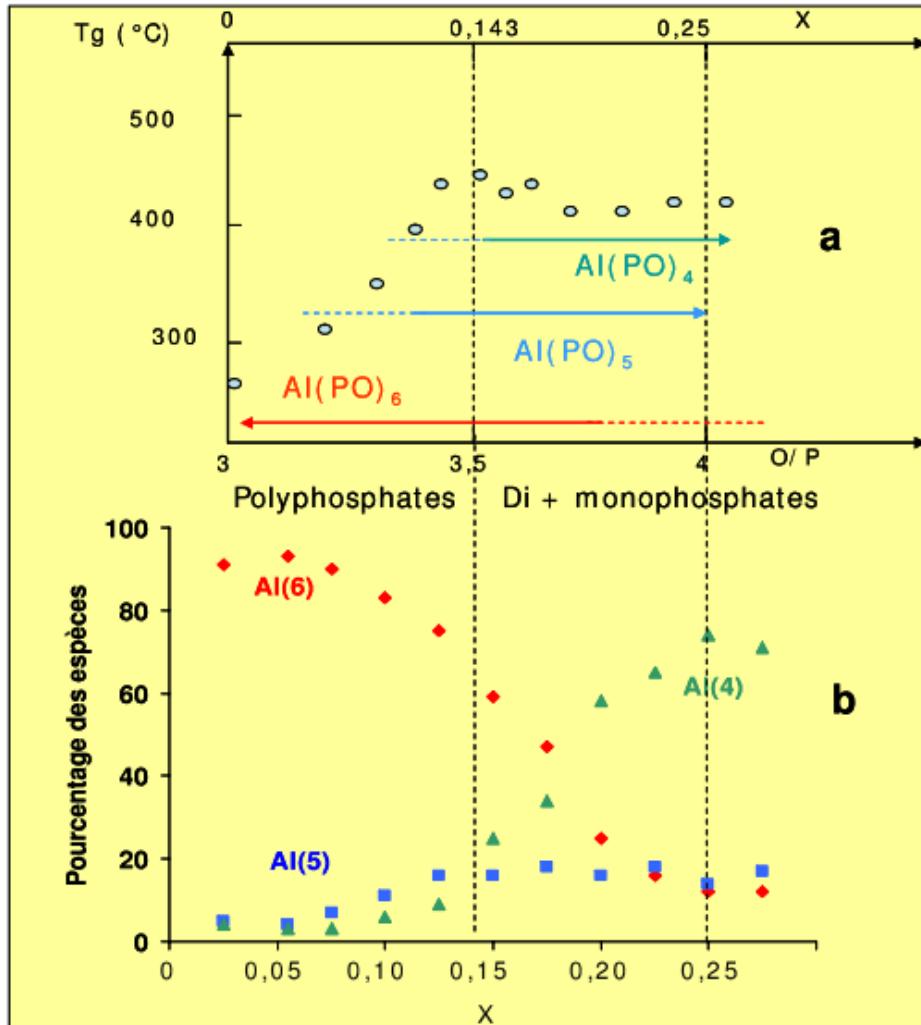
Brow JNCS (1990)
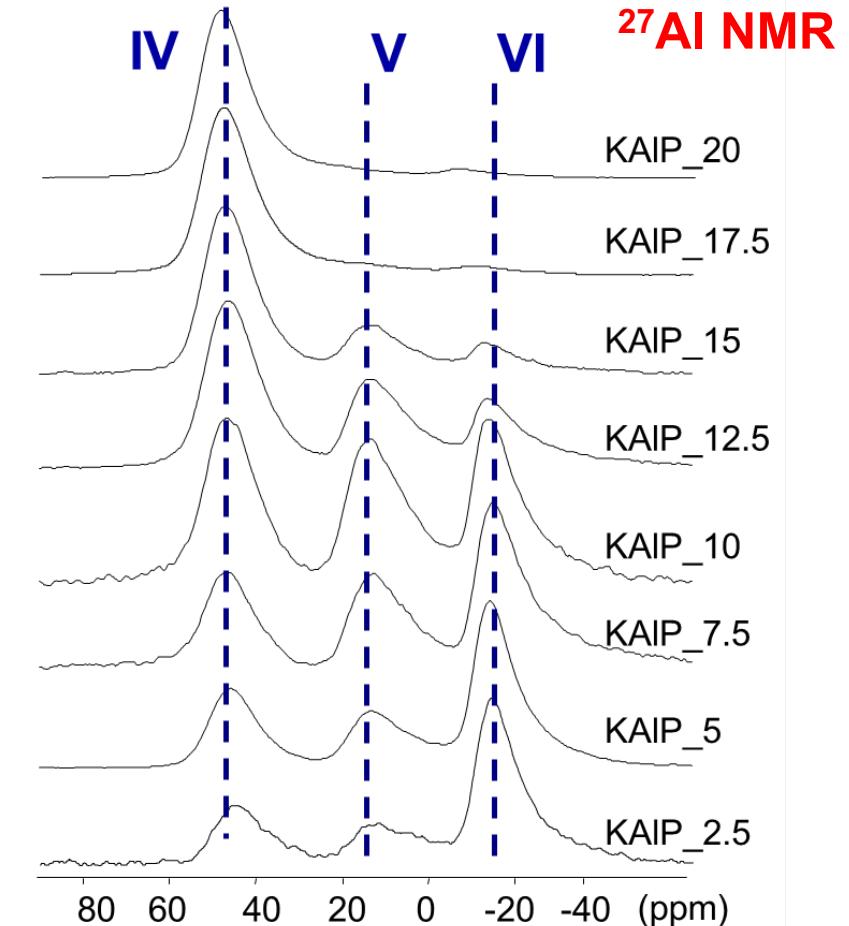
Van Wullen ss-nmr (2007)

Characterization of aluminophosphate glass network: 2D NMR « toolbox »
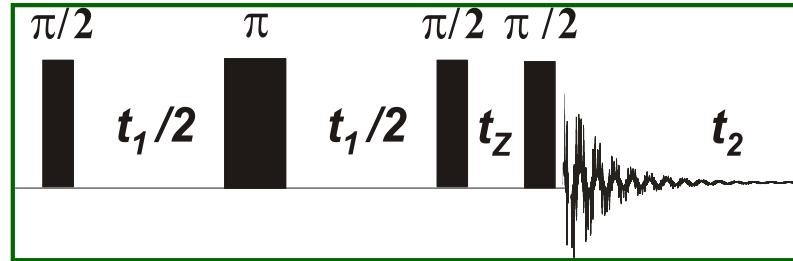
^{31}P J-RESolved
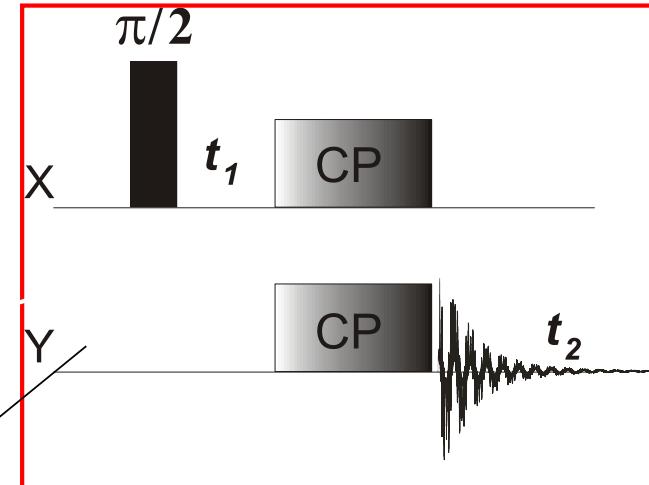
^{31}P {^{27}Al} CP-HETCOR
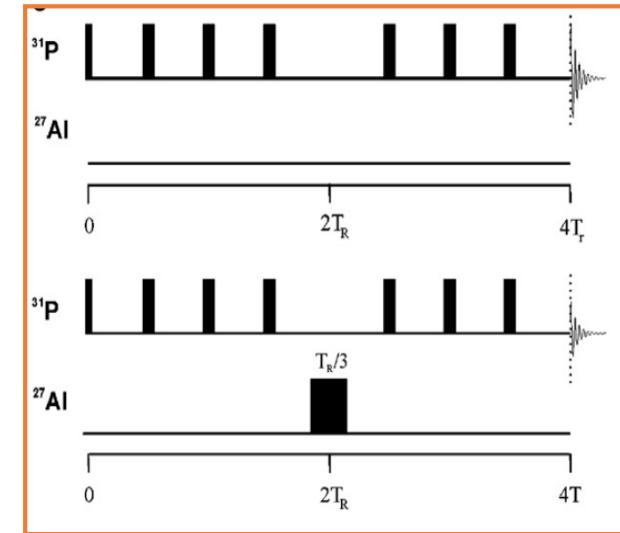
^{31}P {^{27}Al} REAPDOR

$Q^n_{m}, AlOx$

(a)

(b)

(c)

NMR enables an accurate description of the aluminophosphate mixed-network glass

NMR enables an accurate description of the aluminophosphate mixed-network glass

Q^1_0

Q^2_0

$Q^1_{1, AlO6}$

$Q^1_{2, AlO6}$

$Q^1_{1, AlO4}$

$Al(OP)_6$
$(4Q^1_1 + 2Q^1_2)$

$Al(OP)_4$
$(4Q^1_1)$

a)

δ/ppm (^{31}P)

δ/ppm (^{27}Al)
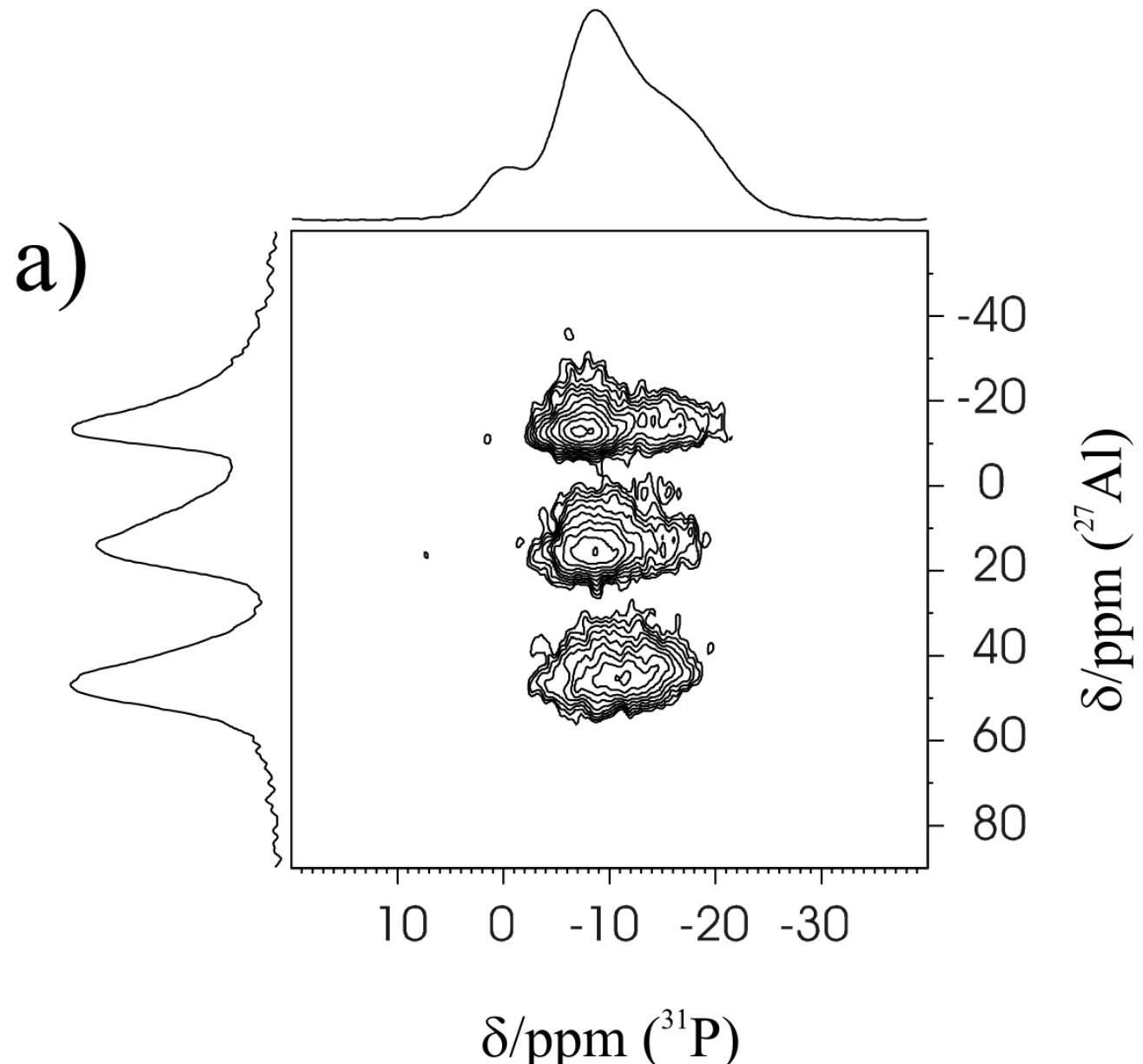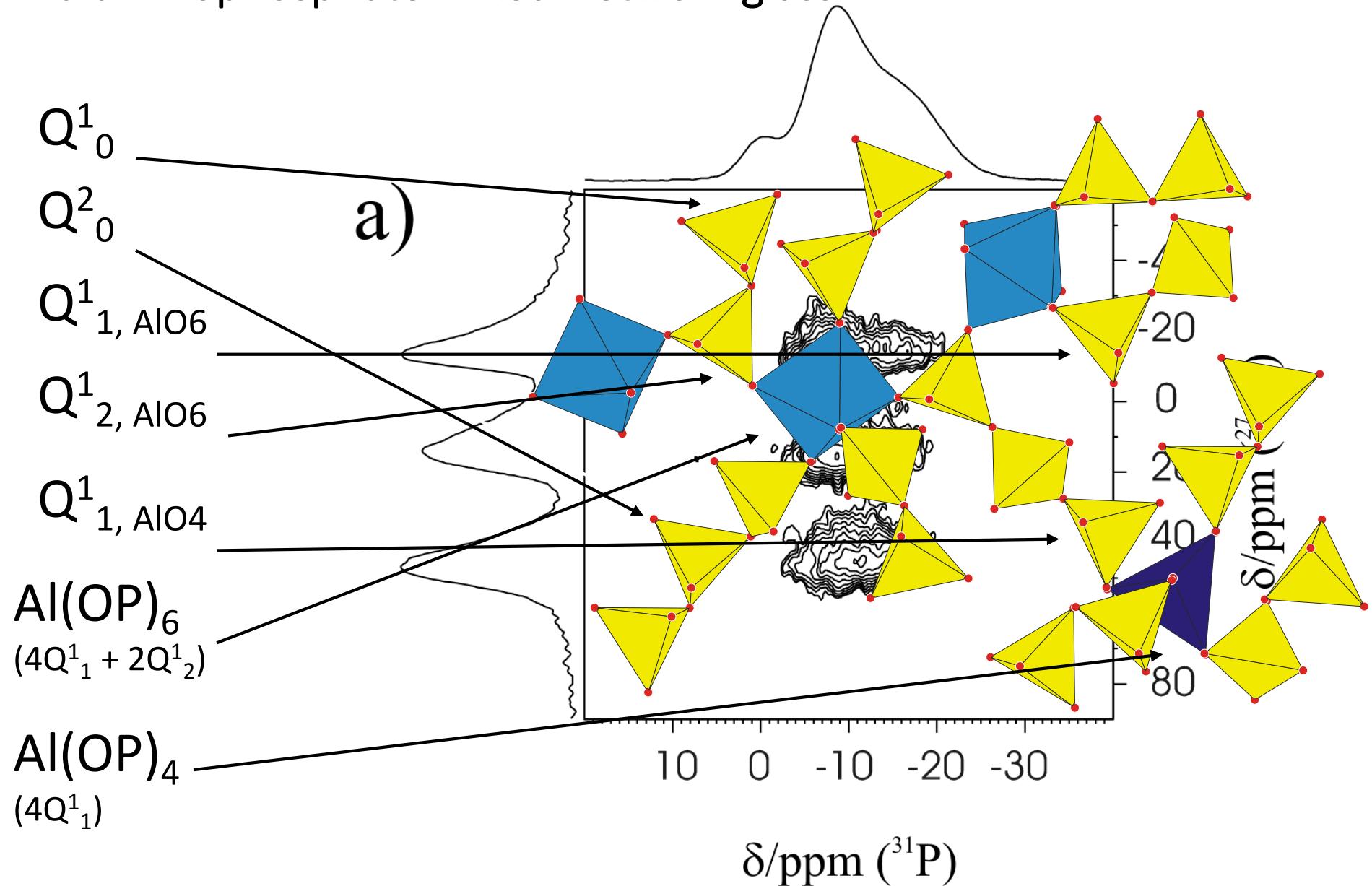
Al(6) then Al(4) : why ?

Valence units (valence/coordinence)
- VU Al(6) = 3/6=0.5, VU Al(4) = 3/4=0.75
- VU Q2 = (5 (P^{5+}) -2(POP))/2 P-O$^-$ bonds = 1.5
- VU Q0 = (5 (P^{5+}))/4 P-O$^-$ bonds = 1.25

=> Al(6) are better stabilized in Q^2

=> Al(4) in less polymerized Q^0 network
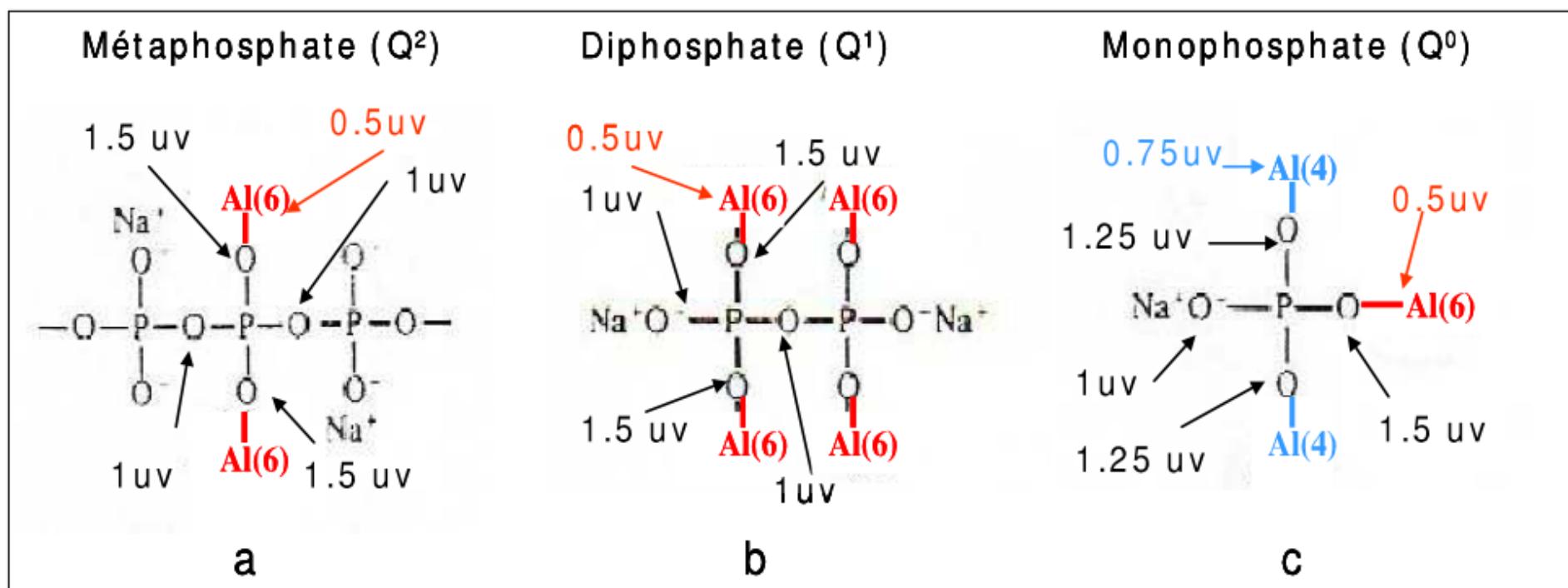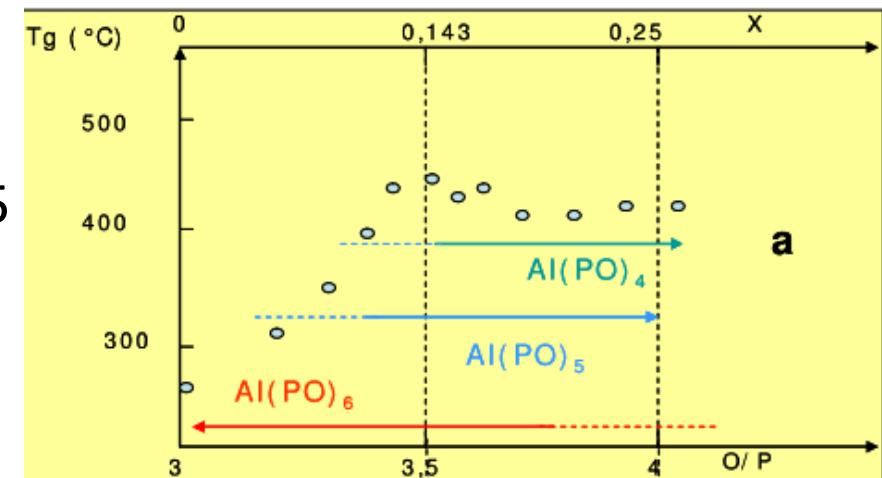
Applications of aluminophosphate glasses
Reticulation => enhanced chemical durability

- Antioxydation coatings for aerospatial composite ceramic materials
- Sealing Glasses
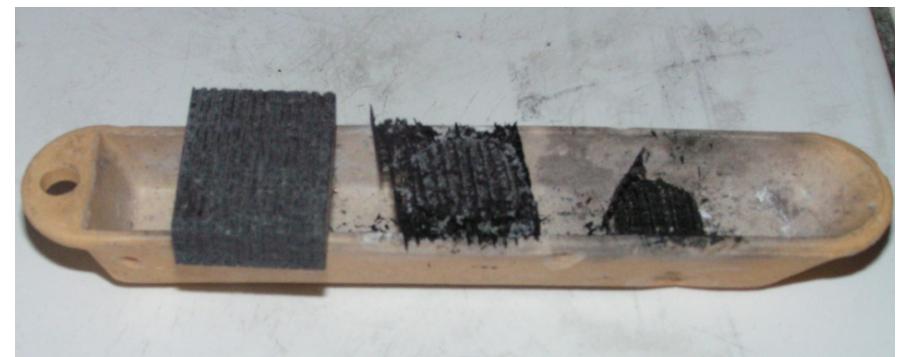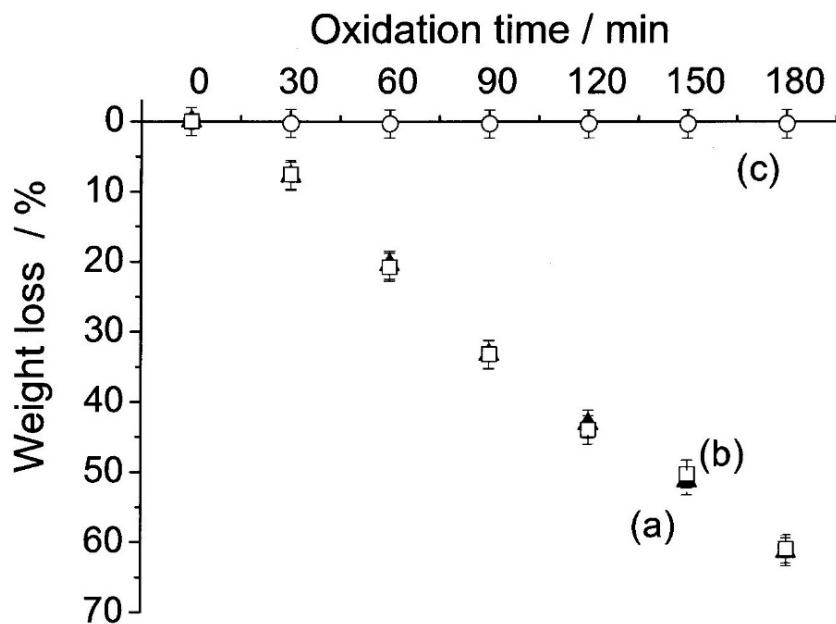
Mixed-network Phosphate glasses for nuclear waste vitrification

- 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

1) Low melting T: ~900-1100 °C;   2) High waste loading;
3) Chemically durable P-O-Fe bonds in glass structure.

8/25   X. Yu et al., J. Non-Cryst. Solids 215, (1997) 21.
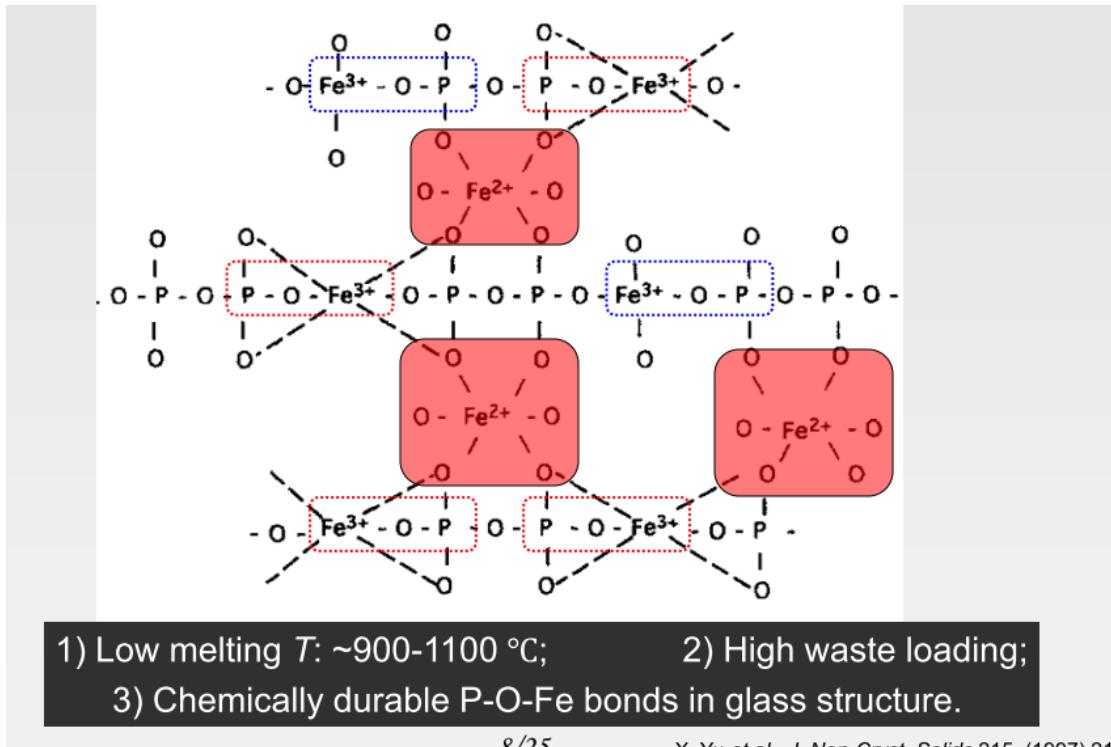
Vapor Hydration Test (VHT)


20
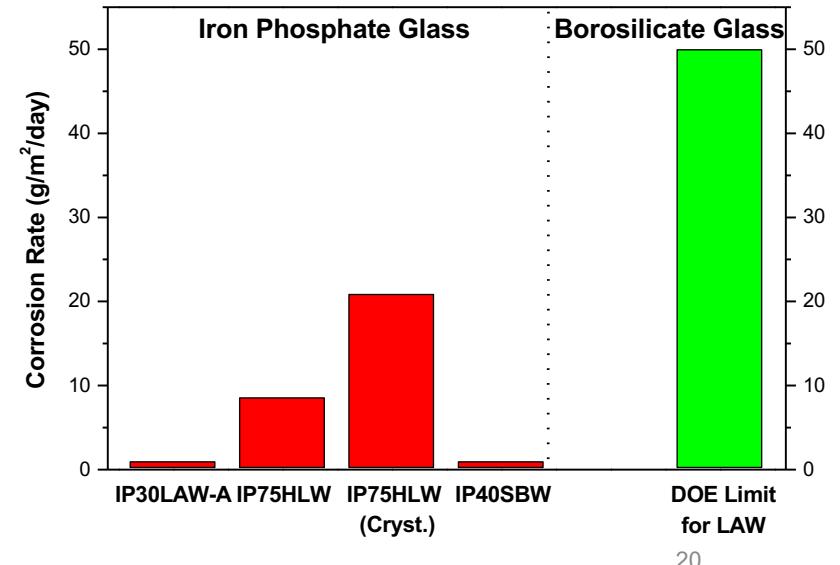
# Transparent Niobiophosphate glass-ceramics
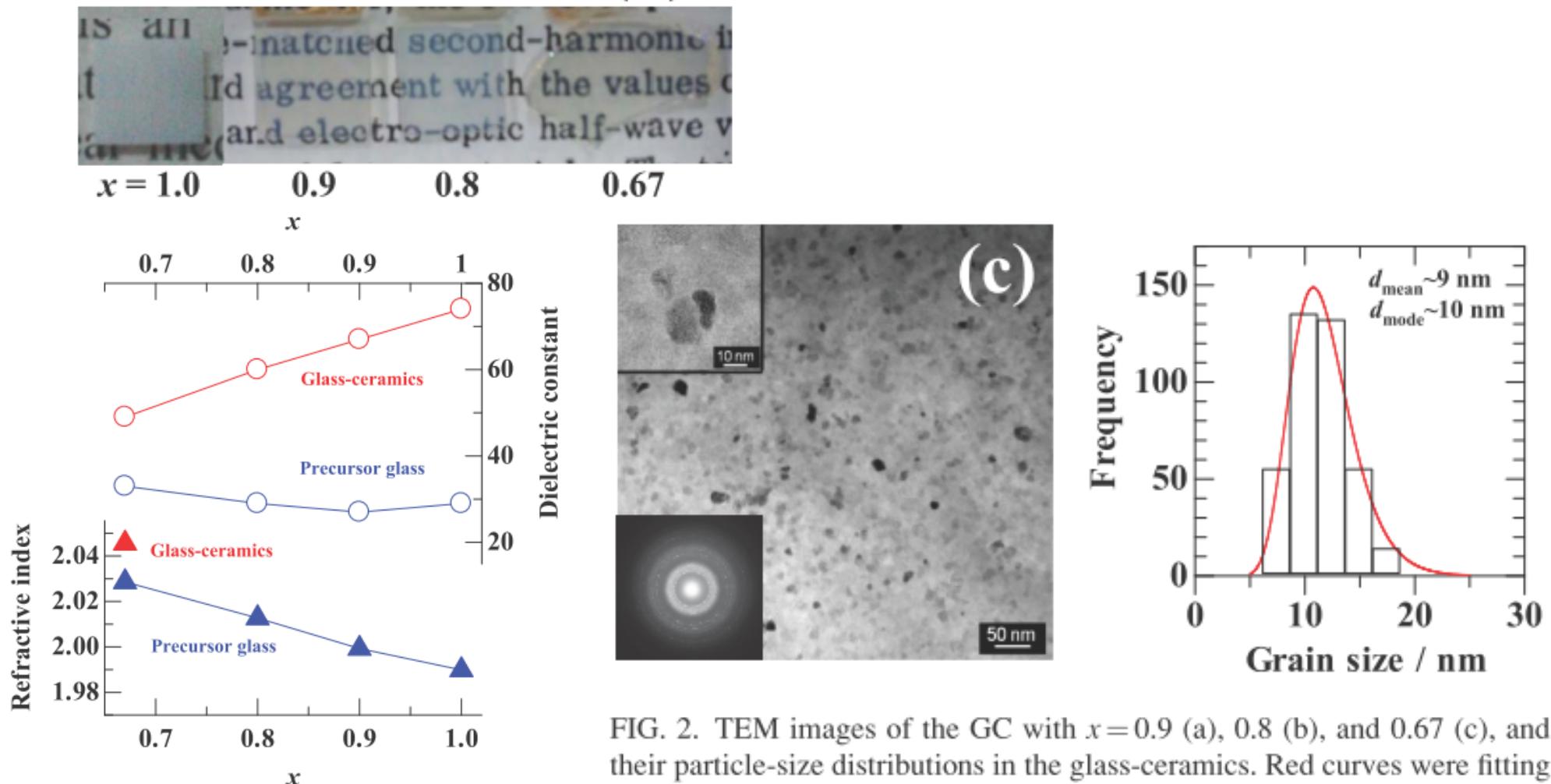
FIG. 2. TEM images of the GC with $x = 0.9$ (a), 0.8 (b), and 0.67 (c), and their particle-size distributions in the glass-ceramics. Red curves were fitting results by log-normal function. d_{mean} and d_{mode} correspond to mean and mode diameters, respectively.

Takahashi, Fujie, and Fujiwara Appl. Phys. Lett. 100, 201907 (2012)

21

# Niobiophosphates glasses : Second harmonic generation for optical switchs

Glass compositions: xNb_2O_5-$(100-x)(95NaPO_3-5Na_2B_4O_7)$

$n_{2SiO_2}=0.6\ 10^{-19}\ m^2/W$

x Nb$_2$O$_5$

x=0.43 n=1.96
x=0.4 n=1.89
x=0.37 n=1.84
x=0.22 n=1.72
x=0.11 n=1.61
x=0 n=1.58

Non-libear index n_2 (m^2/W)

Nb Concentration (mol/m^3)

Q^2 Q^1 Q^0

Q^1exp

Q^2exp Q^0exp

% Q^n

O/P
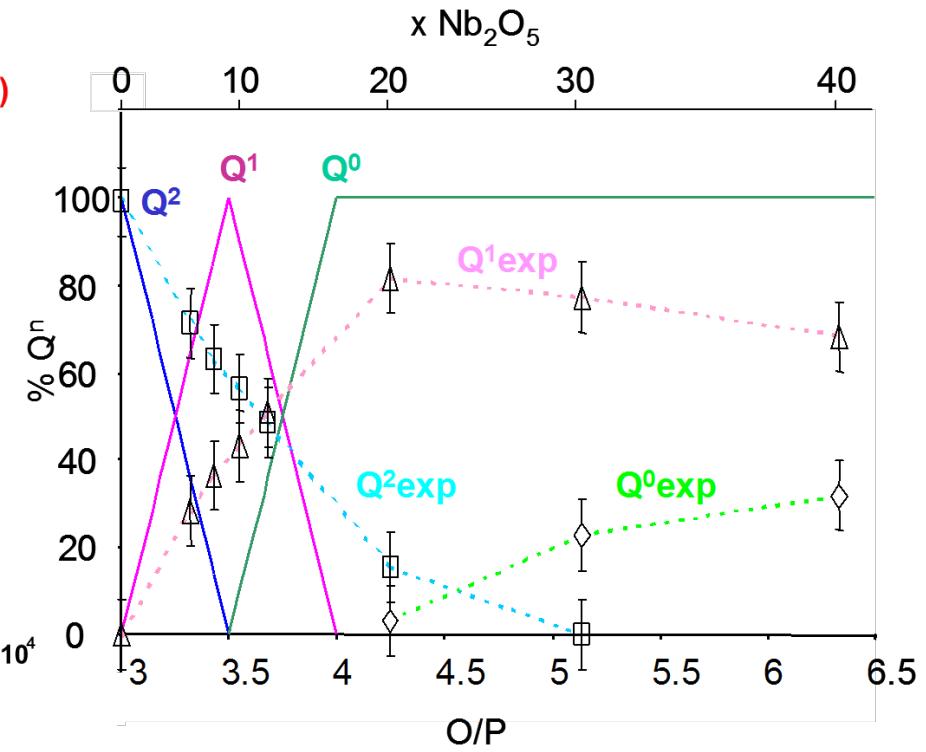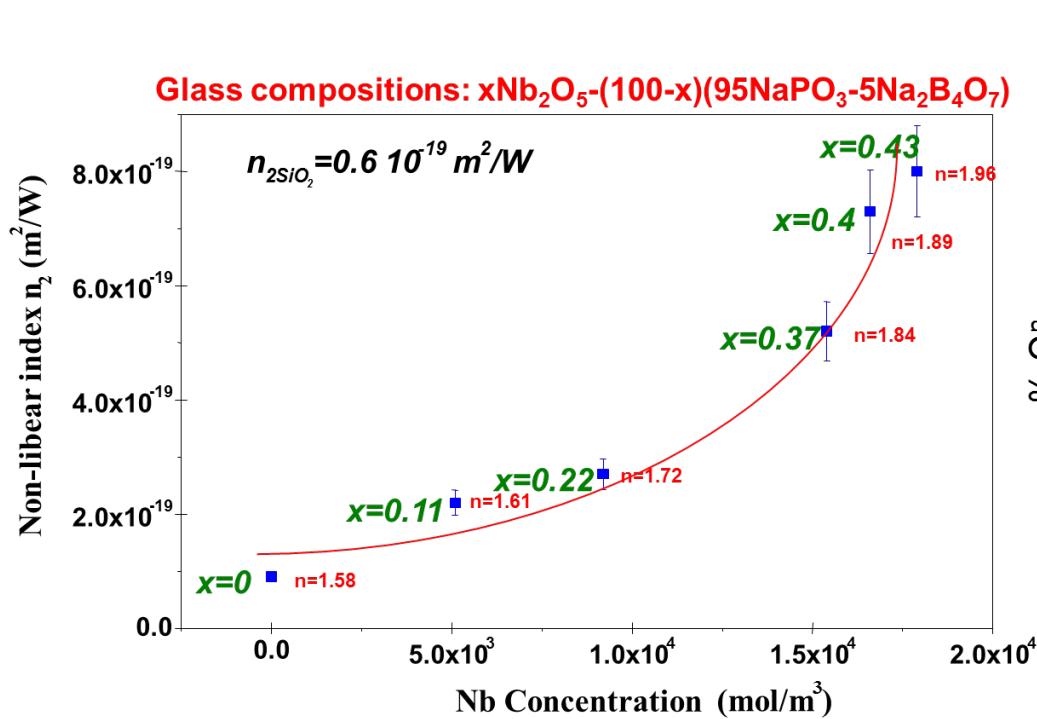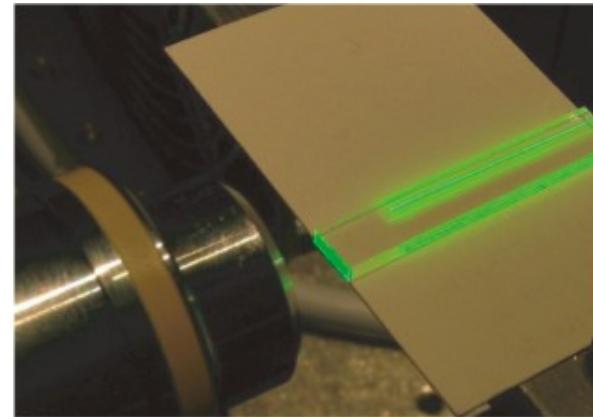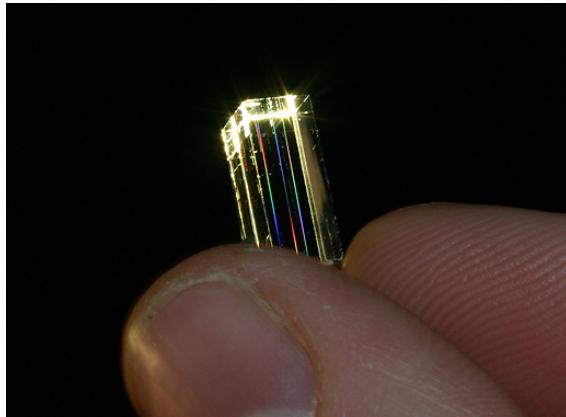
T. Cardinal, ICMCB

Property vs. structure

$0 < x < 20$

$Q^2 + Q^1$, **Nb(OP)$_6$**
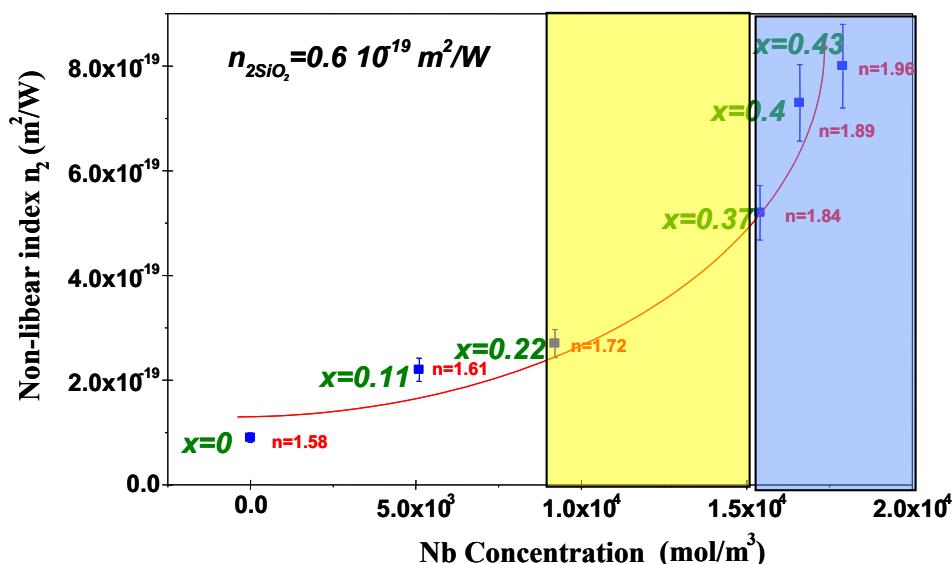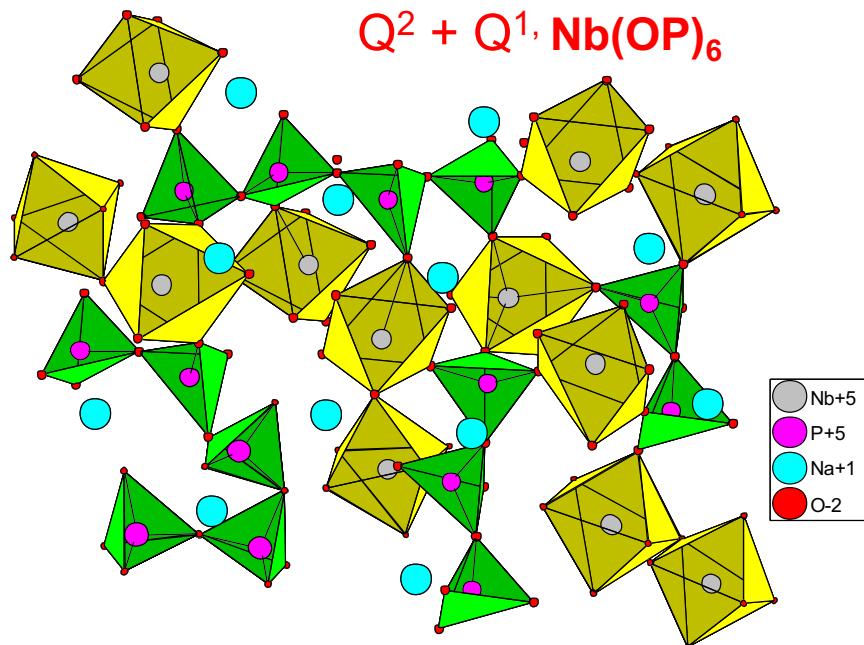
Q^2, $Q^1 + Q^0$
Nb(OP)$_{6-x}$(ONb)$_x$

$20 \leq x < 30$
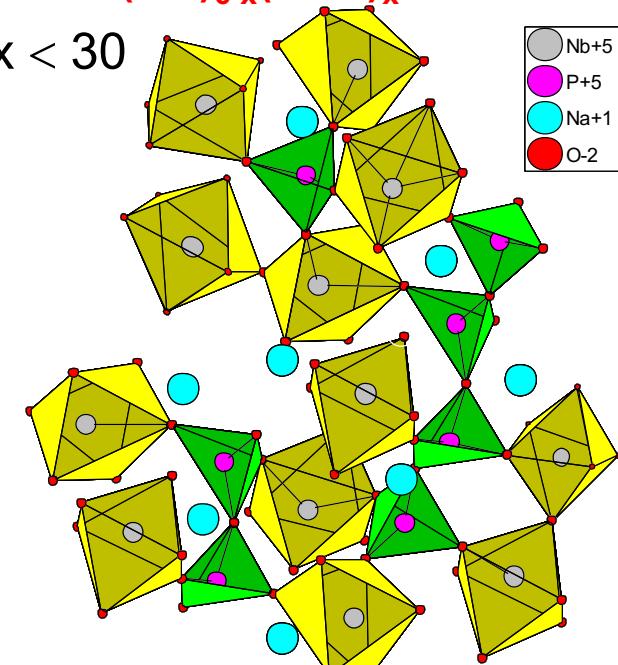
Nb+5
P+5
Na+1
O-2

$x \geq 30$ $Q^1 + Q^0$, **NbO$_6$ clusters**

$n_{2SiO_2} = 0.6 \ 10^{19} \ m^2/W$

x=0.43 n=1.96

x=0.4 n=1.89

x=0.37 n=1.84

x=0.22 n=1.72

x=0.11 n=1.61

x=0 n=1.58

Non-libear index n$_2$ (m^2/W)

8.0×10^{19}
6.0×10^{19}
4.0×10^{19}
2.0×10^{19}
0.0

0.0 5.0×10^3 1.0×10^4 1.5×10^4 2.0×10^4

Nb Concentration (mol/m^3)
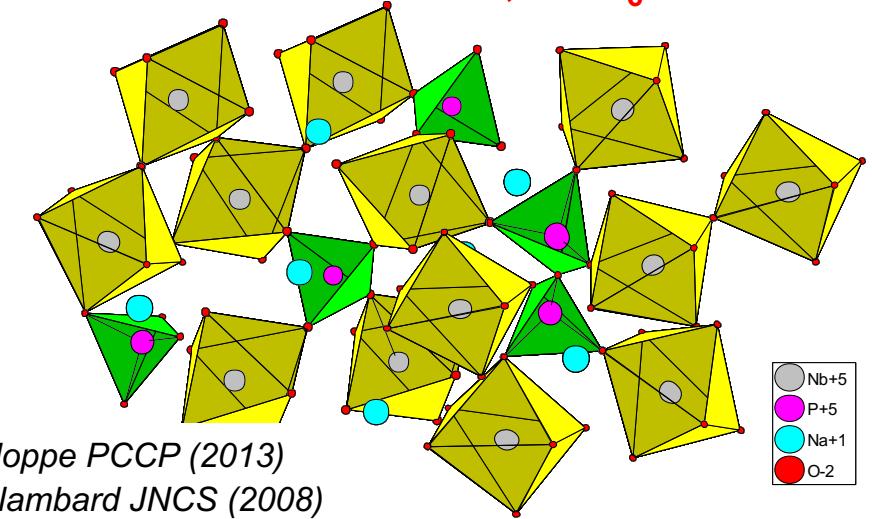
Hoppe PCCP (2013)
Flambard JNCS (2008)

Mixed-network vanadophosphate glasses

Tg versus V_2O_5 content: what we expected…

$\Rightarrow$ % V_2O_5 increases: P network $\rightarrow$ V network

$\Rightarrow$ V_2O_5 network is weaker than P_2O_5 one

$$\begin{cases} \text{Tg } NaPO_3: 285°C \ [1] \\ \text{Tg } NaVO_3: 212°C \ [1] \end{cases}$$
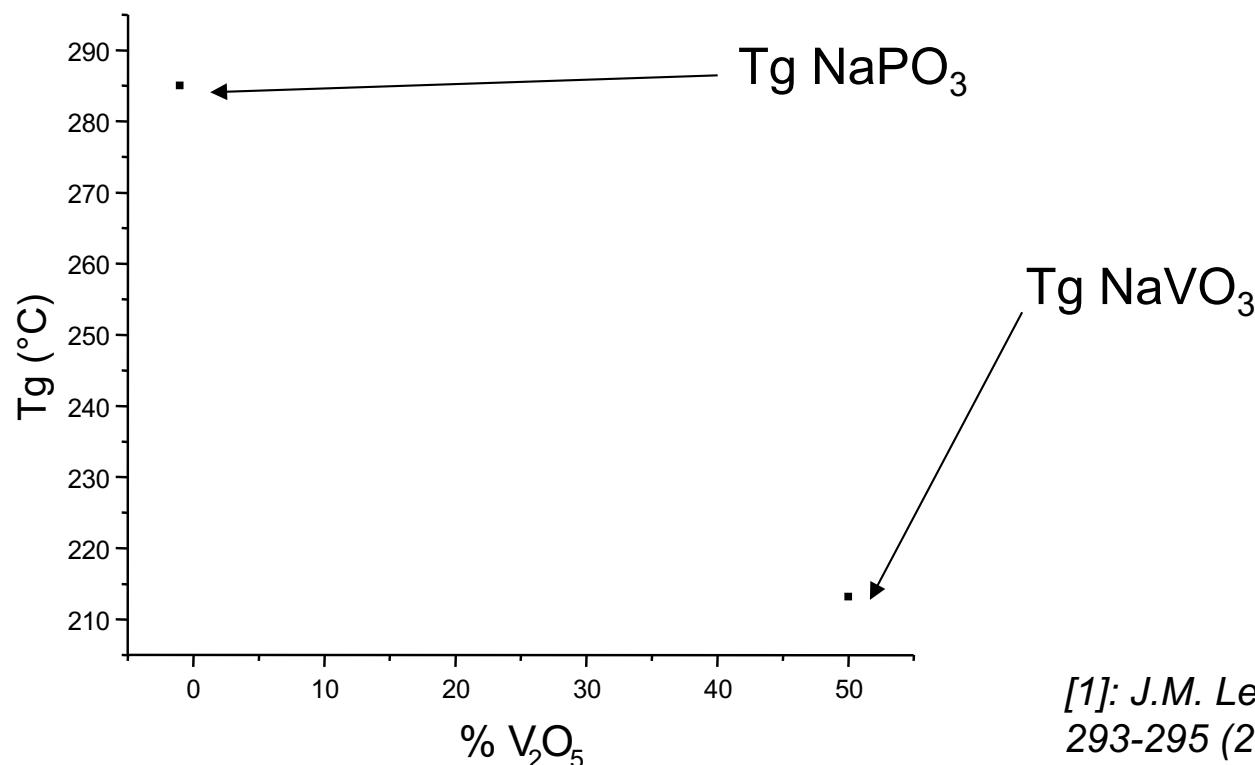
[1]: J.M. Lewis and al. , J-Non Cryst. Solids 293-295 (2001) 663

Tg versus V_2O_5 content: what we obtained…

series 1: $xNaPO_3/(1-x)NaVO_3$

series 2: $xNaPO_3/(1-x)V_2O_5$
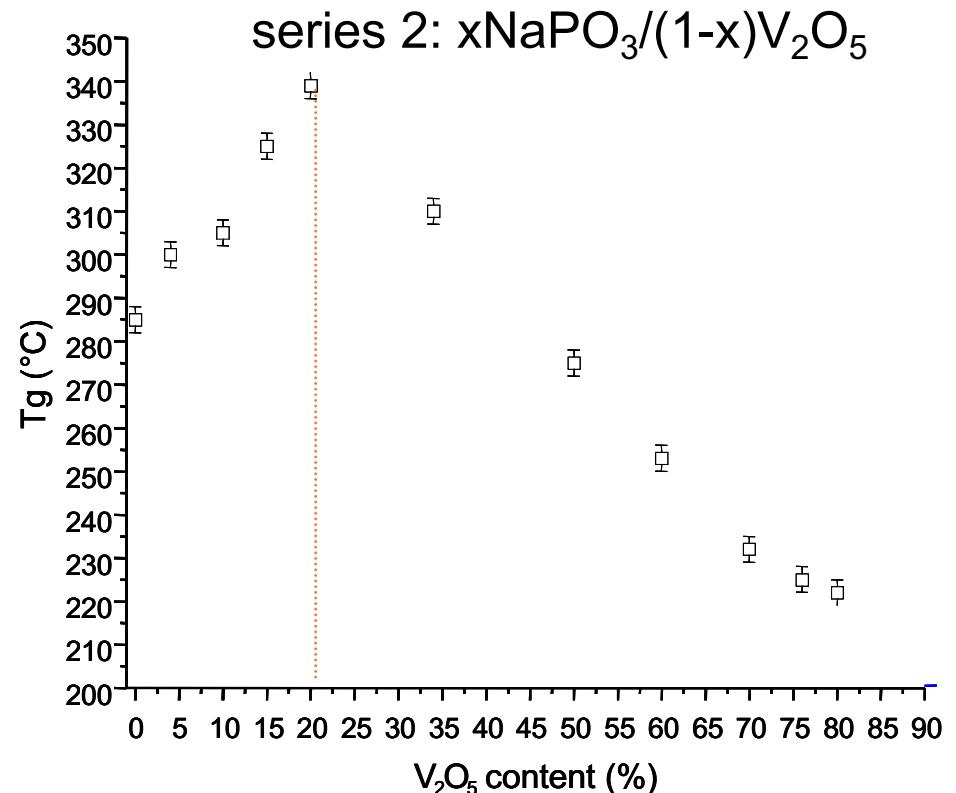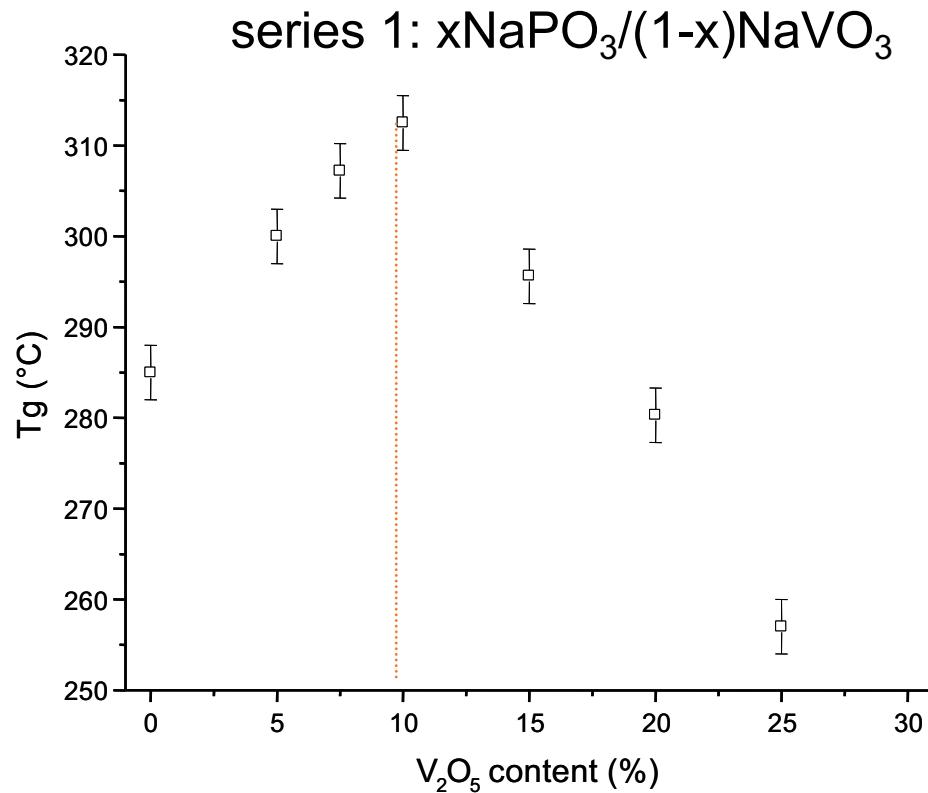
non linear evolution of Tg for the 2 series…

^{31}P NMR of vanadophosphate glasses

^{31}P MAS NMR
9.4T vrot.28kHz
p1: 1µs (π/8) ; d1: 20s

δ=+7ppm : $NaV_{0,66}P_{0,34}O_3$ [3]

V–O–P–O–V (Q^0)

P-O-P → P-O-V deshielding effect on P [2]

V–O–P–O–R (Q^1)

δ=-20ppm : $NaPO_3$

R–O–P–O–R (Q^2)
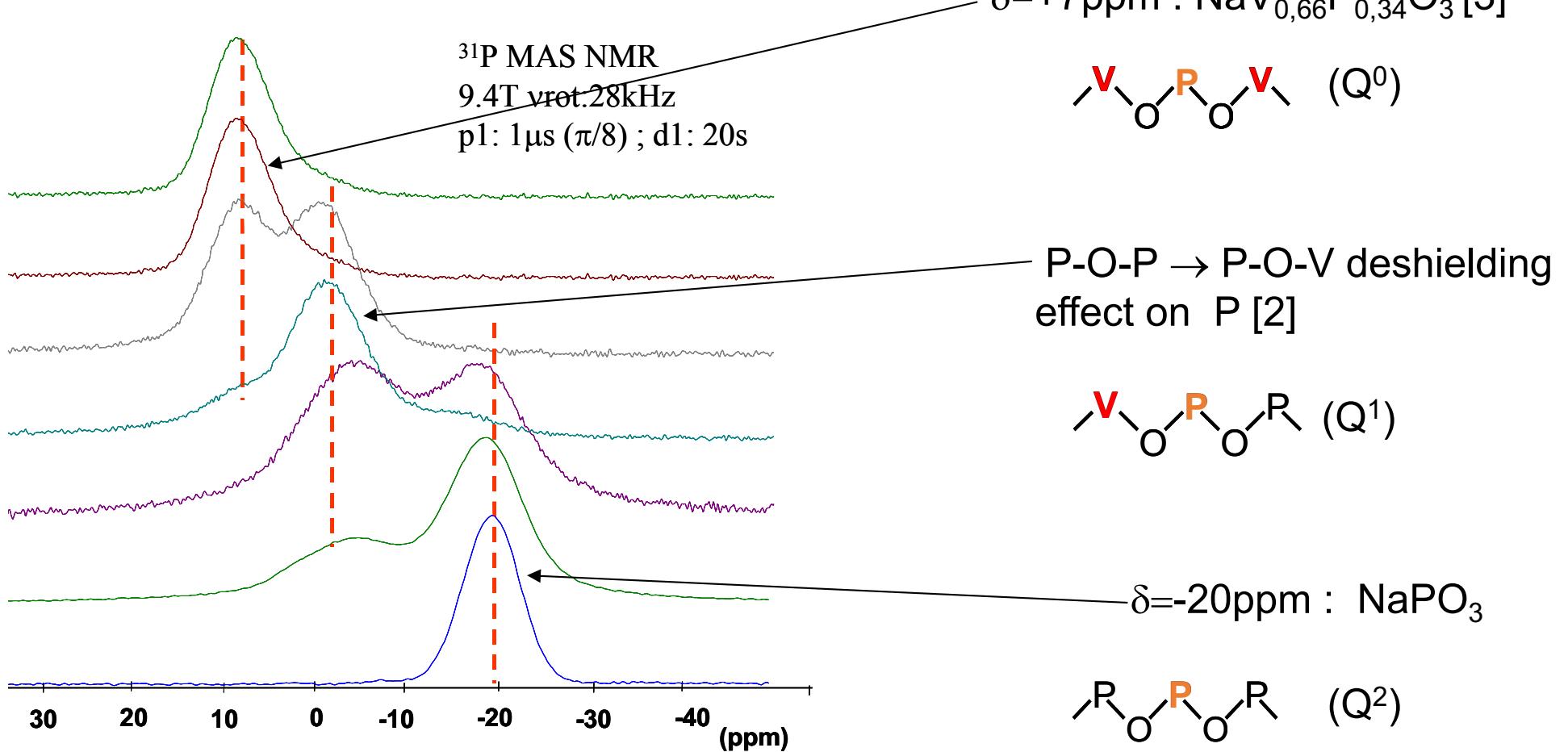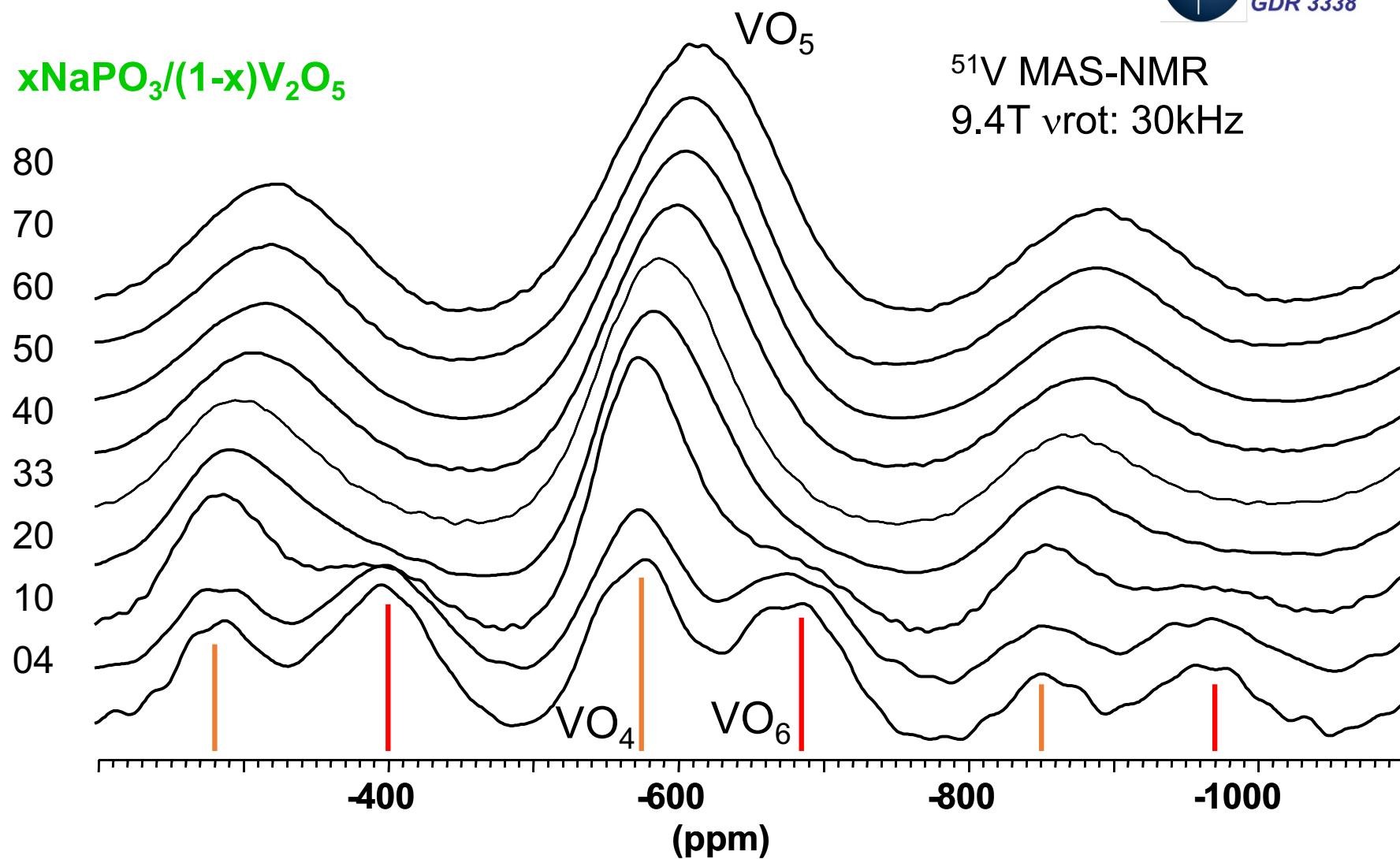
⇒ -580 ppm : CSA (350ppm) : VO_4 [5]

⇒ -680 ppm : large CSA (1000ppm) : VO_6 [5]

[5]: O. Lapina et al, Encyclopedia of NMR vol 8, 4892

Structural considerations explains evolution of properties
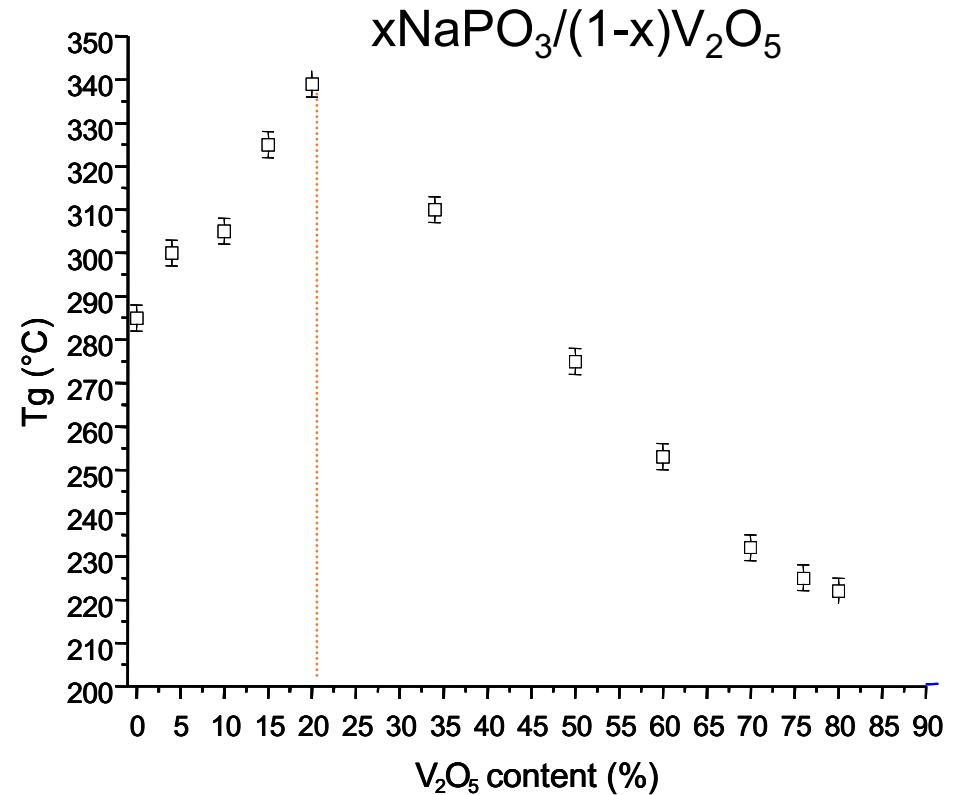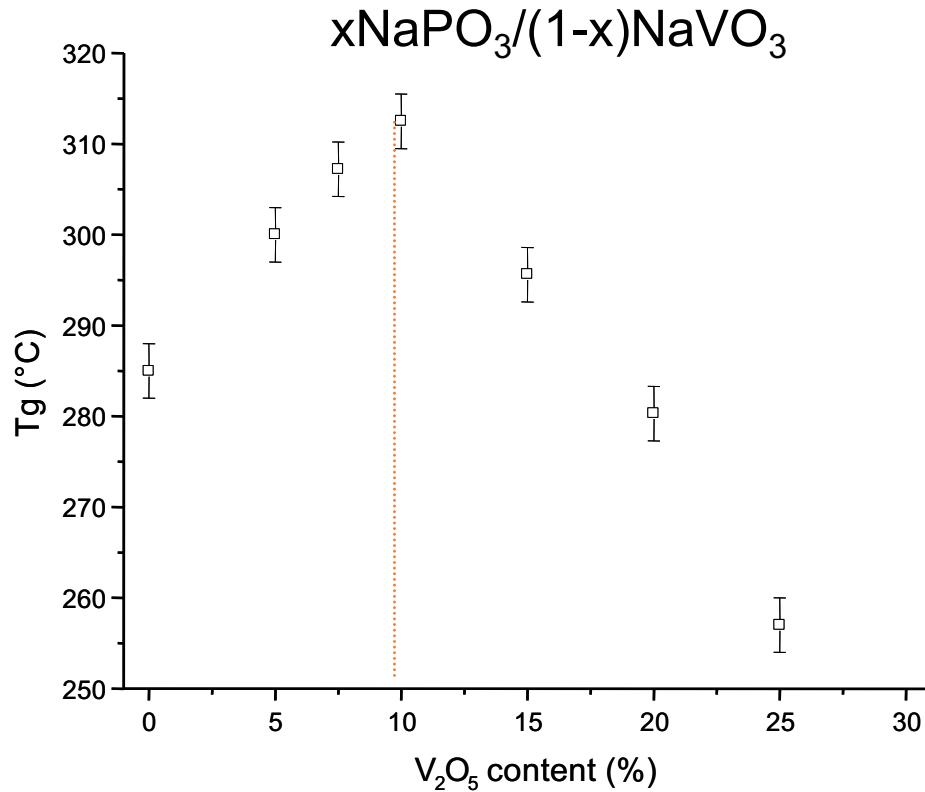
-first domains (Tg increases): reticulation with VO_6
-second domains (Tg decreases): evolution towards a vanadate network

REDOX effect ?

GDR Verres
GDR 3338

xNaPO$_3$/(1-x)NaVO$_3$

xNaPO$_3$/(1-x)V$_2$O$_5$
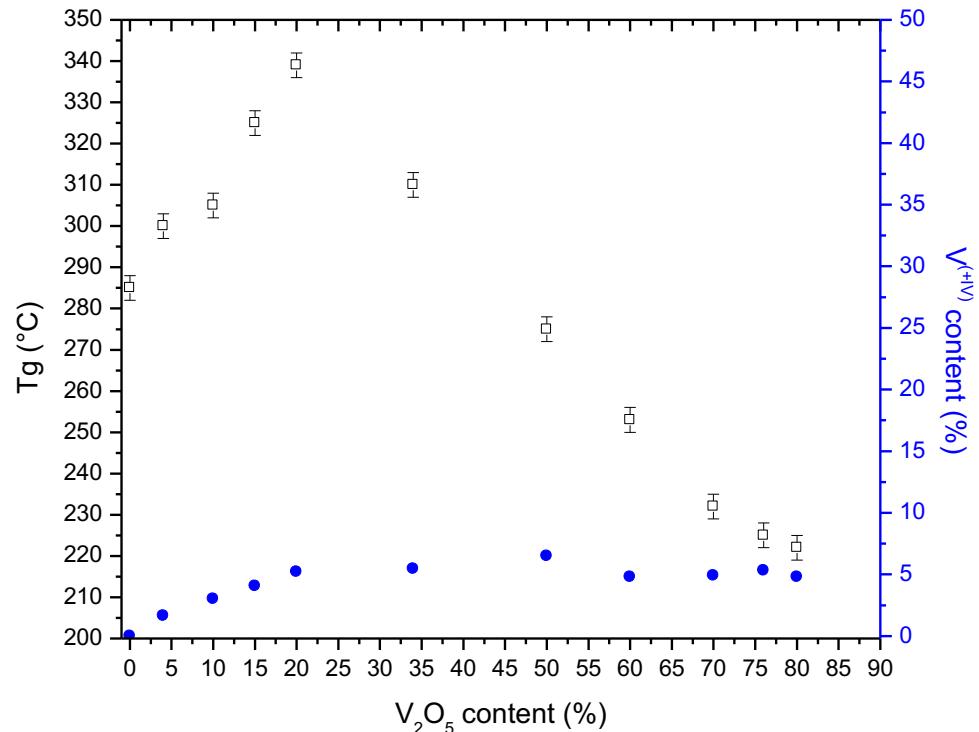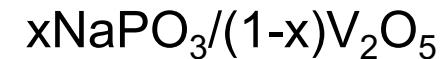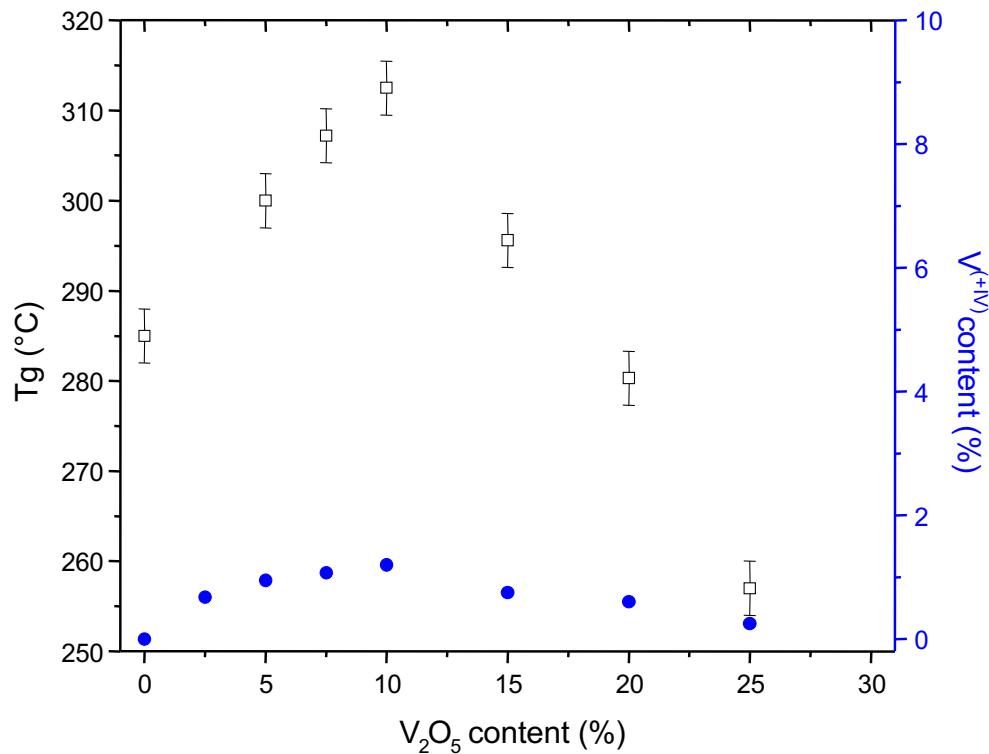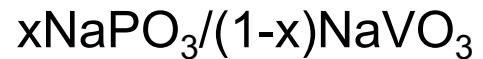
Redox effect on Tg ?
- Quantity of V$^{(+IV)}$ is small
- V$^{(+IV)}$ may contribute to increase Tg at low V$_2$O$_5$ content

Other mixed-network phosphate glasses…

- Borophosphates
- Lead phosphates
- Tin phosphates
- Molybdophosphates
- Silicophosphates

Ducel Phys Chem Glass (1997)
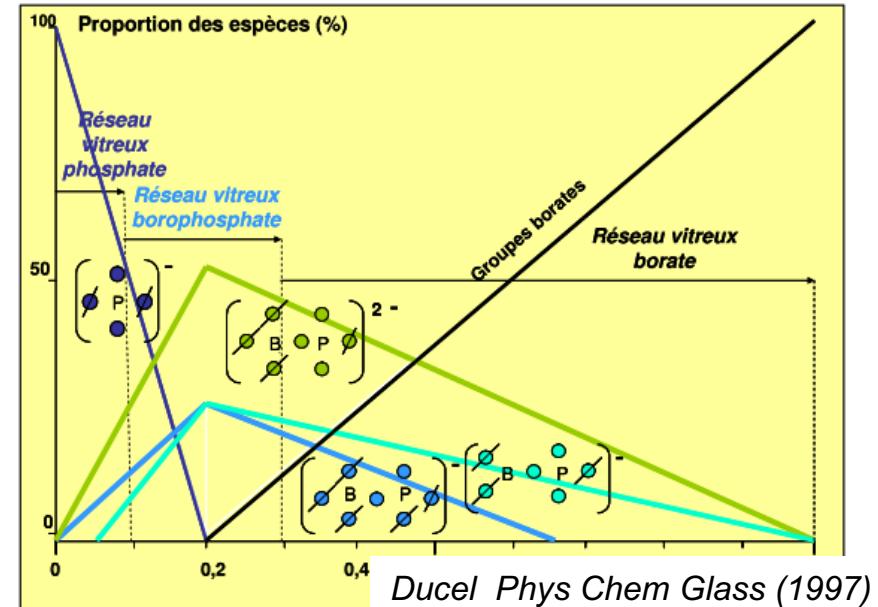
Phosphate glasses: applications are related to network polymerization

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

phosphates

P-O-P

Mixed-networks

P-O-M

Phosphate
network
polymerization

P-F

Fluorophosphates

P-N=

Nitrided phosphates