Spring School GDR Verres, Cargèse 2017

Nitrided (oxynitride) glasses

The origin and concept of nitrided glasses
Methods of preparation. Silicates vs Phosphates
Structure of oxynitride networks
Effect of N on physical and chemical properties
Applications and current developments

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Origin of nitrided glasses

First experiments by Hans-Otto Mulfinger:
Studied **dissolution of N** through bubbling N_2, H_2/N_2 or NH_3 in silicate and borate melts: < 1 wt. % N

(Mulfinger, J. Am. Ceram. Soc. 49 (1966) 462)

Importance of nitrogen in glasses:
Hot pressing of nitrogen containing ceramics to produce SiAlON phases and formation of a **glassy phase at grain boundaries**

(Jack, J. Mat. Sci. 11 (1976) 1135)

Incorporation of nitrogen in phosphate glasses
Thermal ammonolysis of the phosphate melt

(Marchand, CR Acad Sc Paris 294 (1982) 91,
Marchand, J. Non-Cryst. Solids 56 (1983) 173)

CHIMIE DU SOLIDE. — *Mise en évidence de verres de phosphates contenant de l'azote.* Note (*) de **Roger Marchand**, présentée par Erwin-Félix Bertaut.

Pour la première fois ont été mis en évidence des verres de phosphates contenant de l'azote. Par action de l'ammoniac sur le phosphate $NaPO_3$, on a montré l'existence d'un domaine vitreux dans l'intervalle de composition $NaPO_3$-$NaPO_2N_{0,67}$. Pour la composition la plus riche en azote dans laquelle le rapport N/O+N est égal à 0,25, on a précisé les principales caractéristiques.

Synthesis of oxynitride glasses

- Silicate glasses: melting with metallic nitrides

Si_3N_4, AlN, Li_3N, Ca_3N_2, Mg_3N_2 (Hampshire, J. Eur. Ceram. Soc. 28 (2008) 1475
Sharafat, Ceram. Int. 41 (2015) 3345)

La + SiO_2 + Si_3N_4 (Hakeem, Adv. Mat. 17 (2005) 2214)

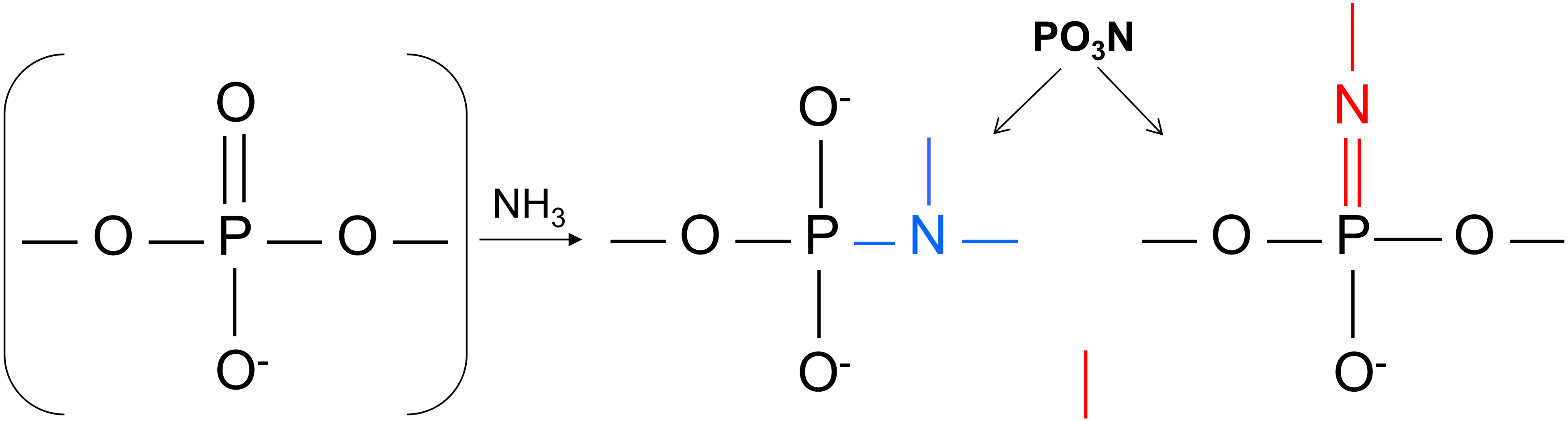
- Phosphate glasses: thermal ammonolysis of phosphate melts

Melting of phosphate glass
+
Thermal treatment in NH_3 flow at T < 800ºC

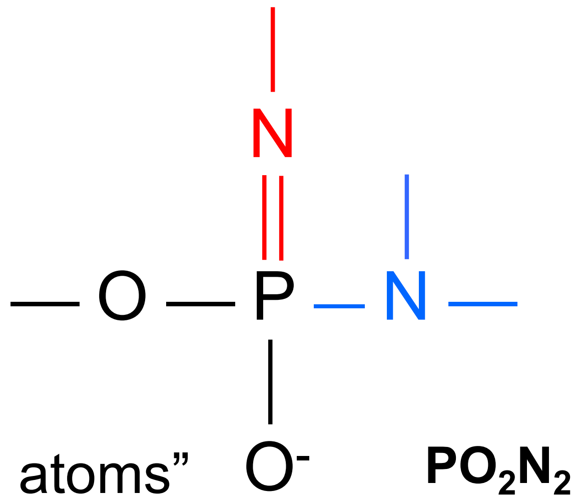
Liquid-gas chemical reaction: $MPO_3 + xNH_3 \rightarrow MPO_{3-3x/2}N_x + 3x/2H_2O$

Substitution of nitrogen for oxygen in phosphates

Improves the chemical resistance
Increases the electrical conductivity
Increases viscosity ⇒ Higher resistance to devitrification

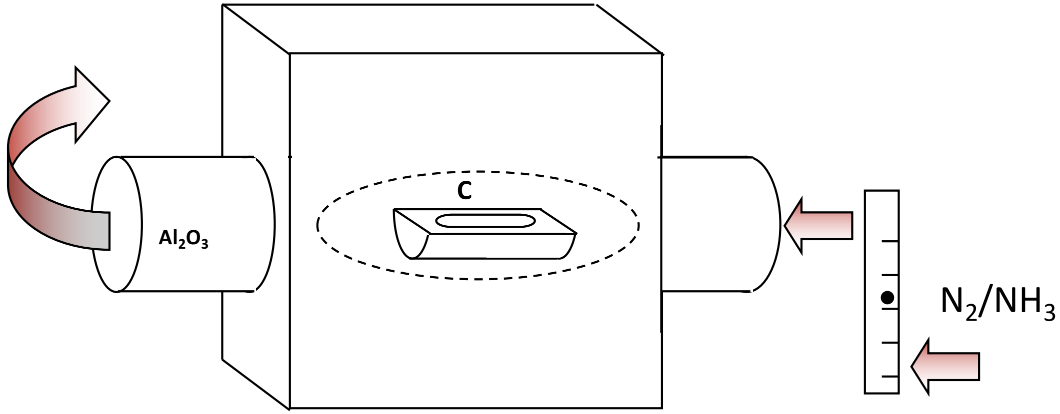


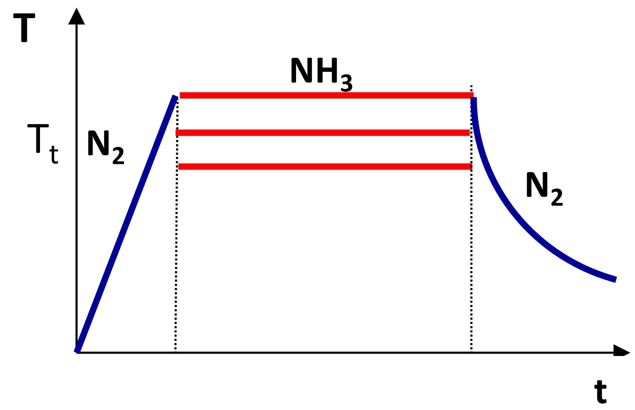
Metaphosphate glass network



Exception to one of Zachariasen’s rules:
“Anions should not bind more than 2 central atoms”
⇒ **Higher degree of interconnected network**

Substitution of nitrogen for oxygen in phosphates





Phosphate glass melting

+

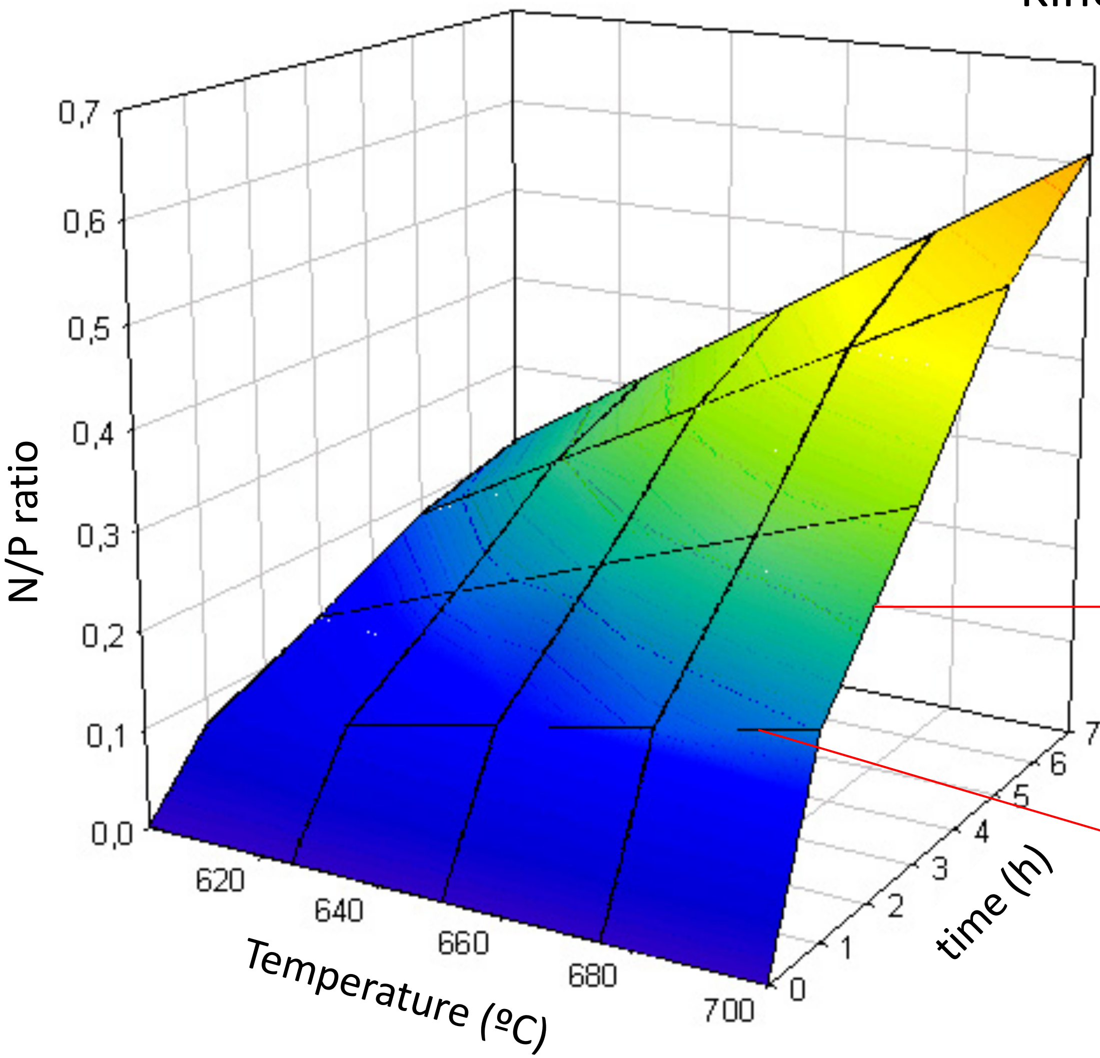
Thermal treatment in NH_3 at T<800ºC

Liquid-gas chemical reaction

$MPO_3 + xNH_3 \rightarrow MPO_{3-3x/2}N_x + 3x/2H_2O$

Substitution of nitrogen for oxygen in phosphates

Kinetics in $\mathbf{LiNaPbPO_{3-3x/2}N_x}$ glasses



$N/P = K_T \cdot \sqrt{t}$

$N/P \propto T$

F. Muñoz *et al., Phys. Chem. Glasses* 43C (2002) 113; F Muñoz 52(4) (2011) 181

Substitution of nitrogen for oxygen in phosphates

Substitution rules by Marchand:

$$N_t = 3/2\ B$$

$$N_d = NBO + 1/2BO$$

$$2PO4 + NH3 \longrightarrow PO3N\text{-}PO3N$$

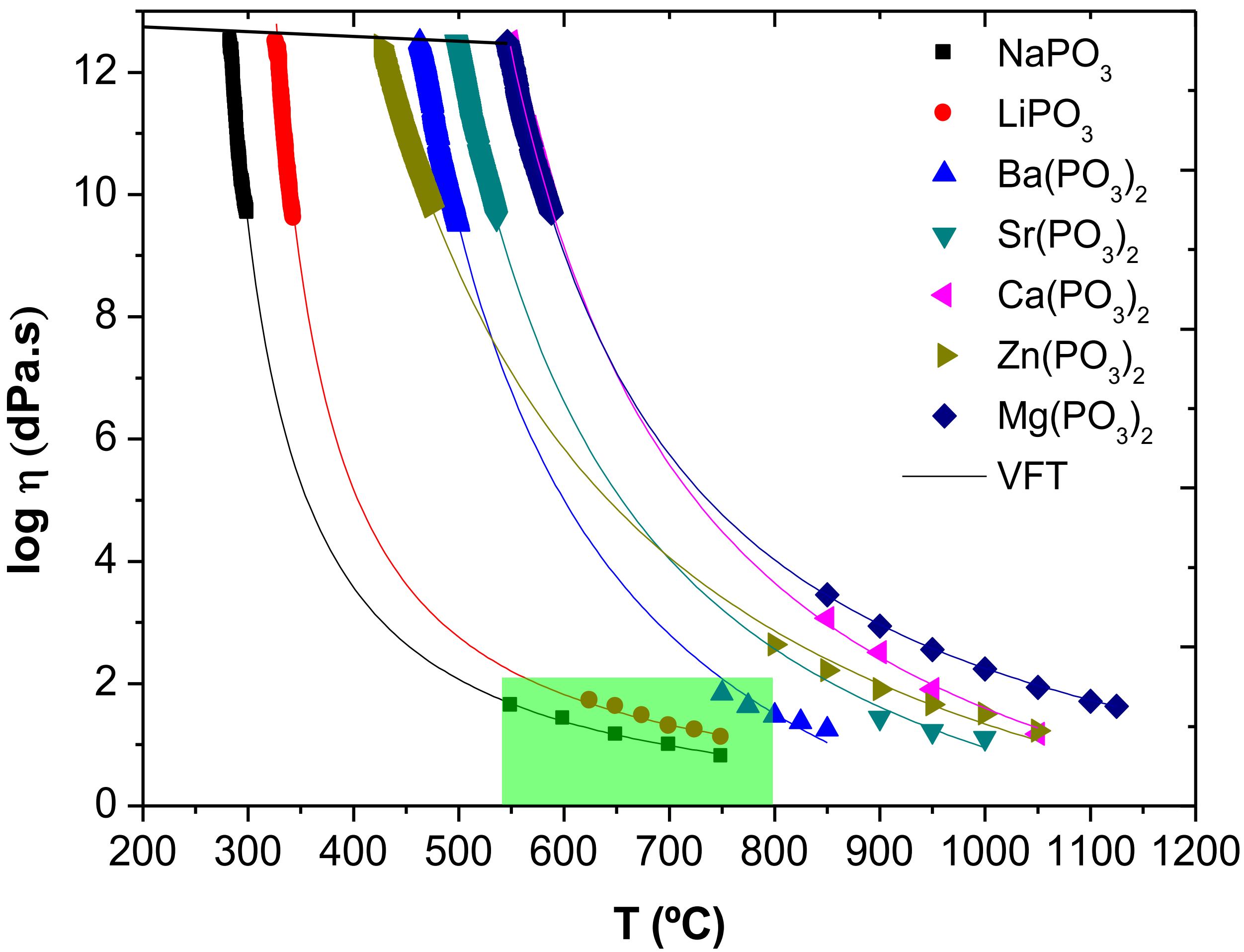
$$PO4 + PO3N + NH3 \longrightarrow PO2N2\text{-}PO3N$$

System of 2 pseudo-first order consecutive reactions

F. Muñoz *et al., Phys. Chem. Glasses* 43C (2002) 113; F Muñoz 52(4) (2011) 181

Substitution of nitrogen for oxygen in phosphates

Muñoz-Senovilla *et al.*, J. Non-Cryst. Solids 385 (2014) 9-14



$NaPO_3$
$LiPO_3$

$LiNaPO_3$
$LiZnPO_3$

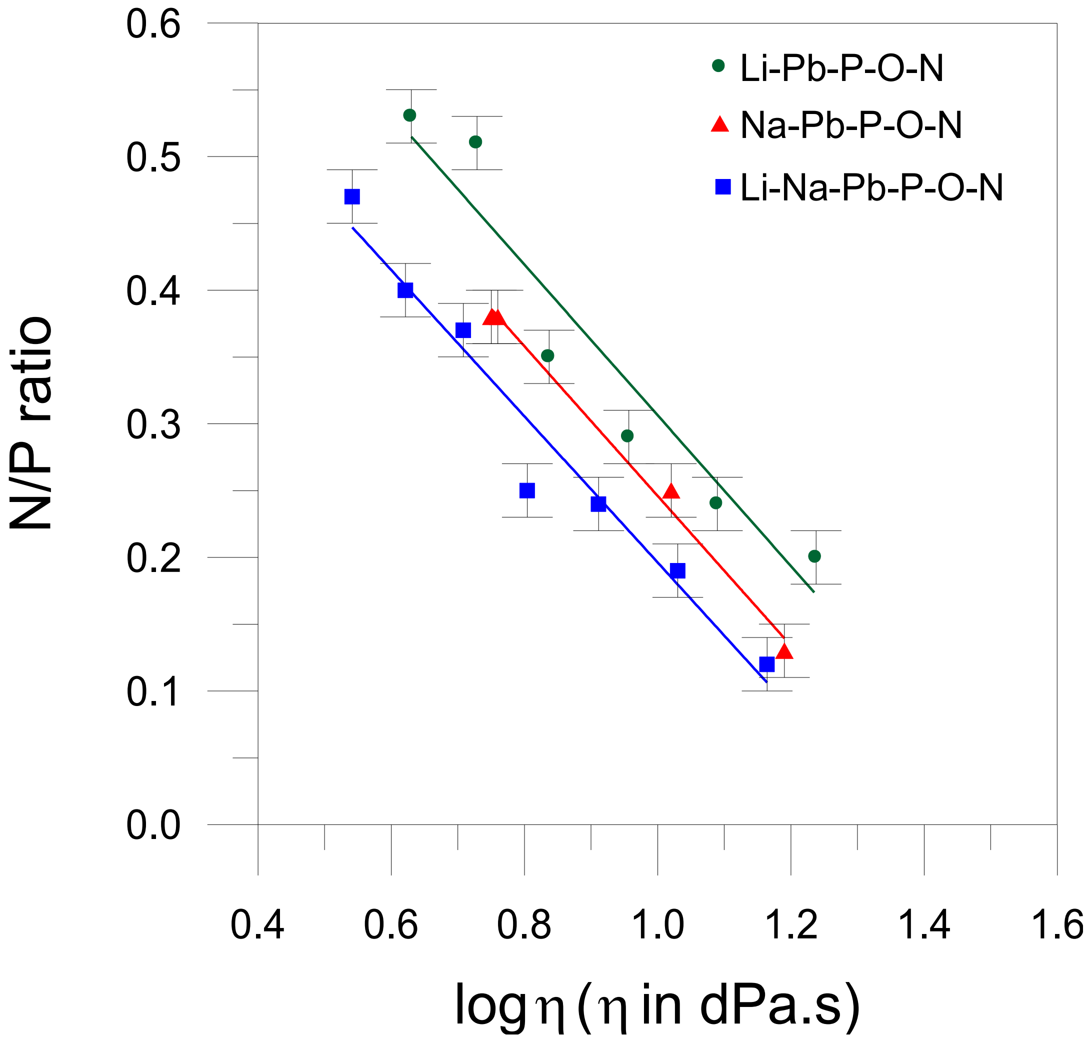
Alkali+akaline-earth

Substitution of nitrogen for oxygen in phosphates

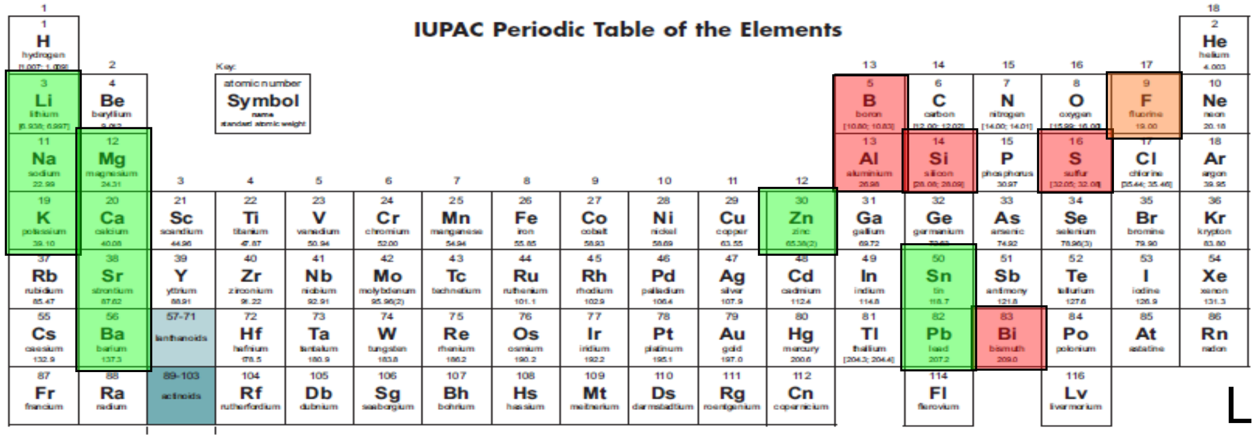
Parameters controlling nitrogen incorporation:

Viscosity of the phosphate melt at the temperature of ammonolysis

Ionic Field Strength (z/r^2)of the modifier cations



Substitution of nitrogen for oxygen in phosphates



- Alkali and alkaline-earth elements:
  No problem provided the melt viscosity is low

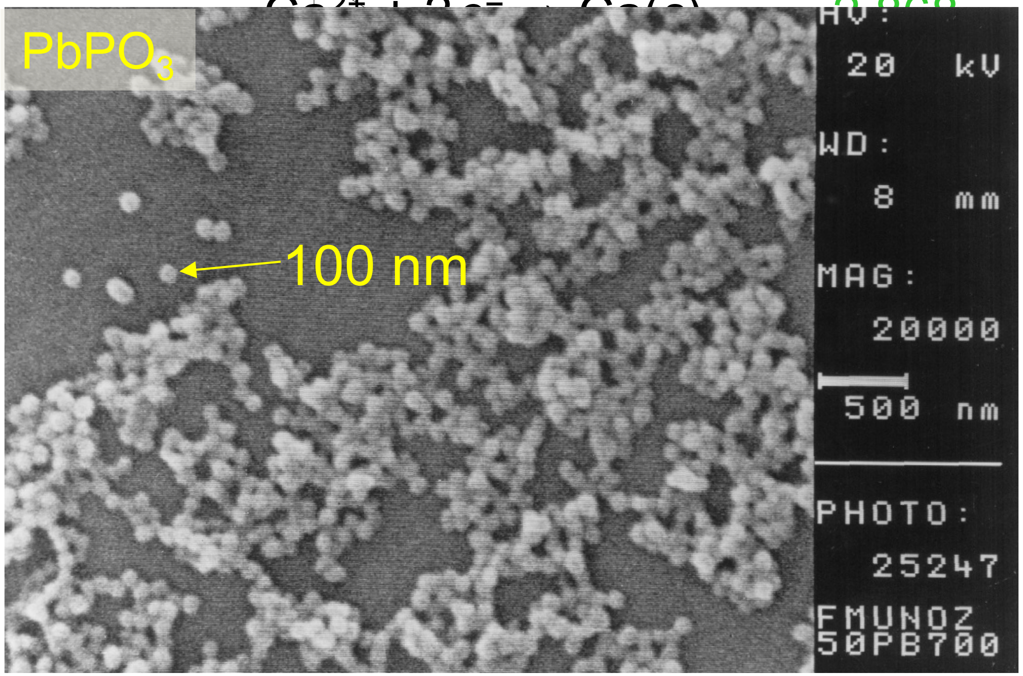
- Former elements:
SiO_2 and Al_2O_3 increase reaction T
B_2O_3 lowers the N content, may form BN

- Volatiles: S^{2-}, F^-, SO_4^{2-} (reduced)

- Metals:
Dependence on their reduction Eº
Precipitation of Cu, Ag, Au
$Sn^{4+} \rightarrow Sn^{2+}$
$Pb^{2+} \rightarrow$ Pb possible in $PbPO_3$

	E°(V)
$Li^+ + e^- \rightarrow Li(s)$	−3.0401
$Na^+ + e^- \rightarrow Na(s)$	−2.71
$Ba^{2+} + 2e^- \rightarrow Ba(s)$	−2.912

N_2 in $(50-x)Na_2O.xB_2O_3.P_2O_5$
700ºC 0.5 h



Structure of oxynitride glasses

Structure of oxynitride glasses

^{29}Si NMR

Koroglu *et al.*, Phys. Chem. Glasses 52 (2011) 175

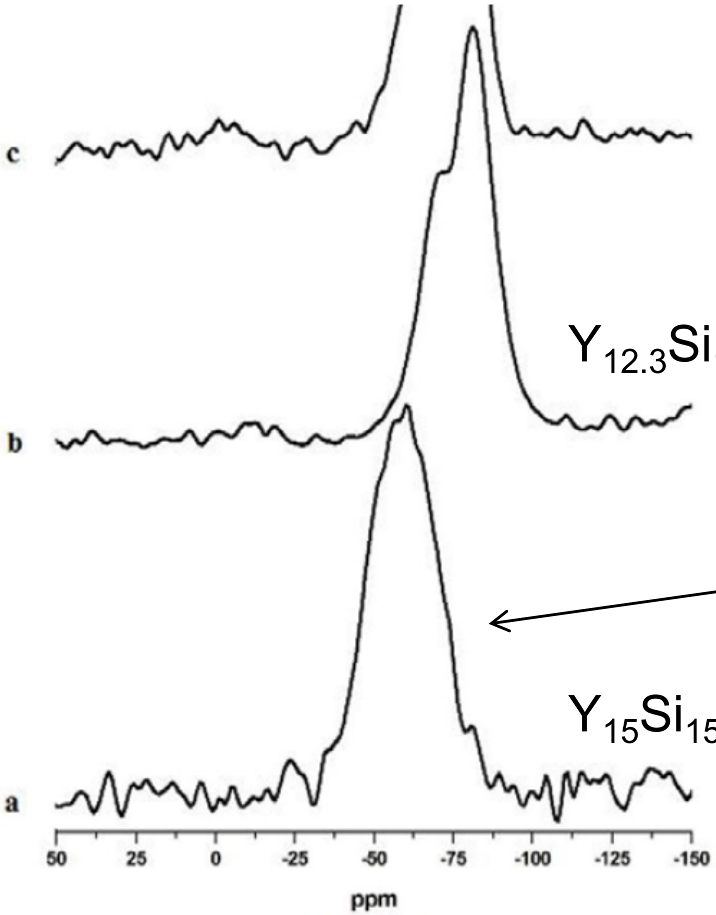


Figure 1. ^{29}Si spectra of samples (a) SMP03, (b) SMP05, (c) SMP06, (d) SMP07 and (e) SMP08

$Y_{12.3}Si_{18.5}Al_{7.1}O_{54.2}{}^{15}N_{7.9}$

$Y_{15}Si_{15}Al_{10}O_{45}{}^{15}N_{15}$

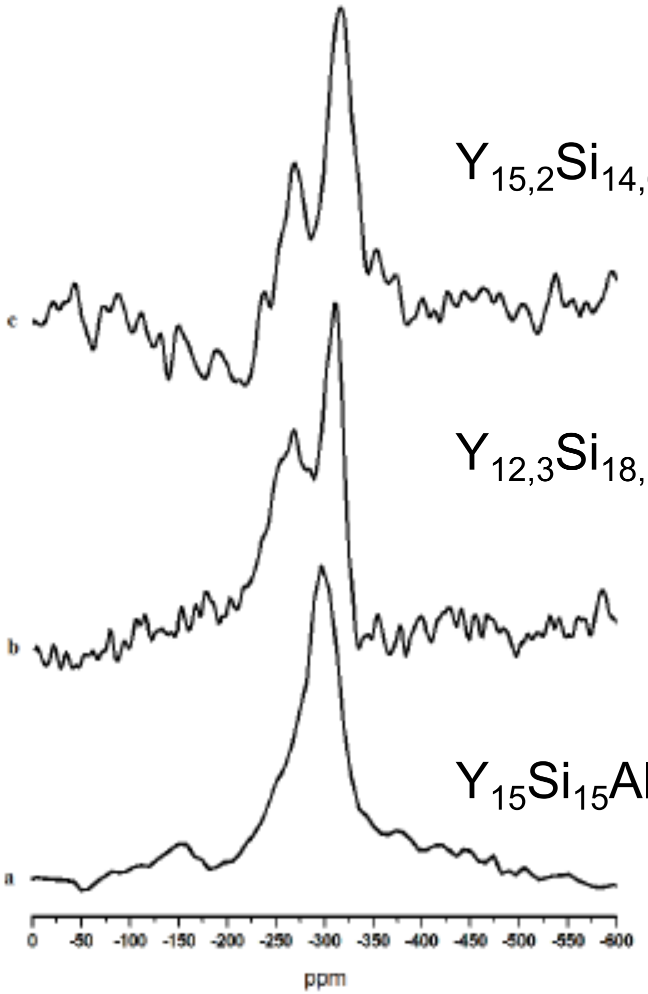
-47, -52, -60, -70, -81 ppm:

SiN_4 (impurities from melting)
SiN_3O
SiN_2O_2
$SiNO_3$
SiO_4

Structure of oxynitride glasses

^{15}N NMR (I=-1/2, 0,37%,4.10^{-6}), needing enrichment in ^{15}N

Koroglu *et al.*, Phys. Chem. Glasses 52 (2011) 175



$Y_{15,2}Si_{14,6}Al_{8,7}O_{54,7}{}^{15}N_{6,9}$

$Y_{12,3}Si_{18,5}Al_{7,1}O_{54,2}{}^{15}N_{7,9}$

$Y_{15}Si_{15}Al_{10}O_{45}{}^{15}N_{15}$

%N

Figure 3. ^{15}N spectra of samples (a) SMP03, (b) SMP05 and (c) SMP01

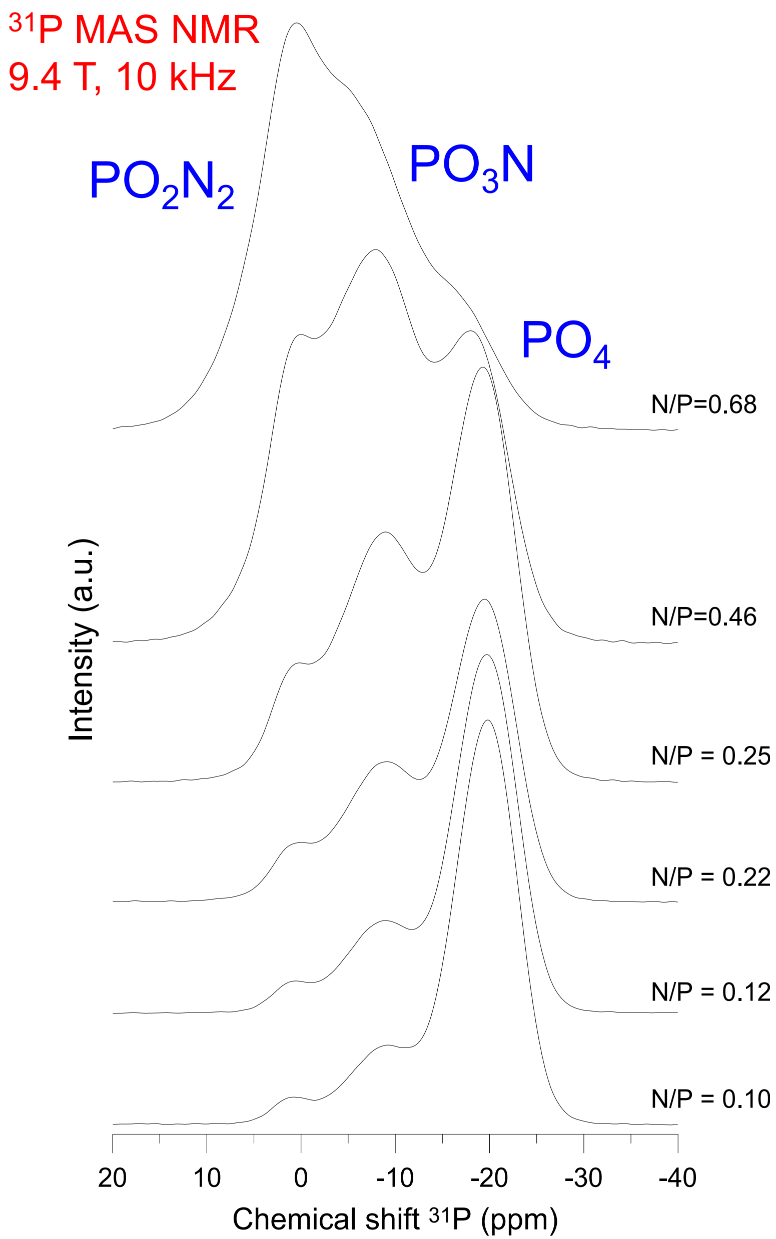
-268 ppm: NSi_2

Si–N=Si

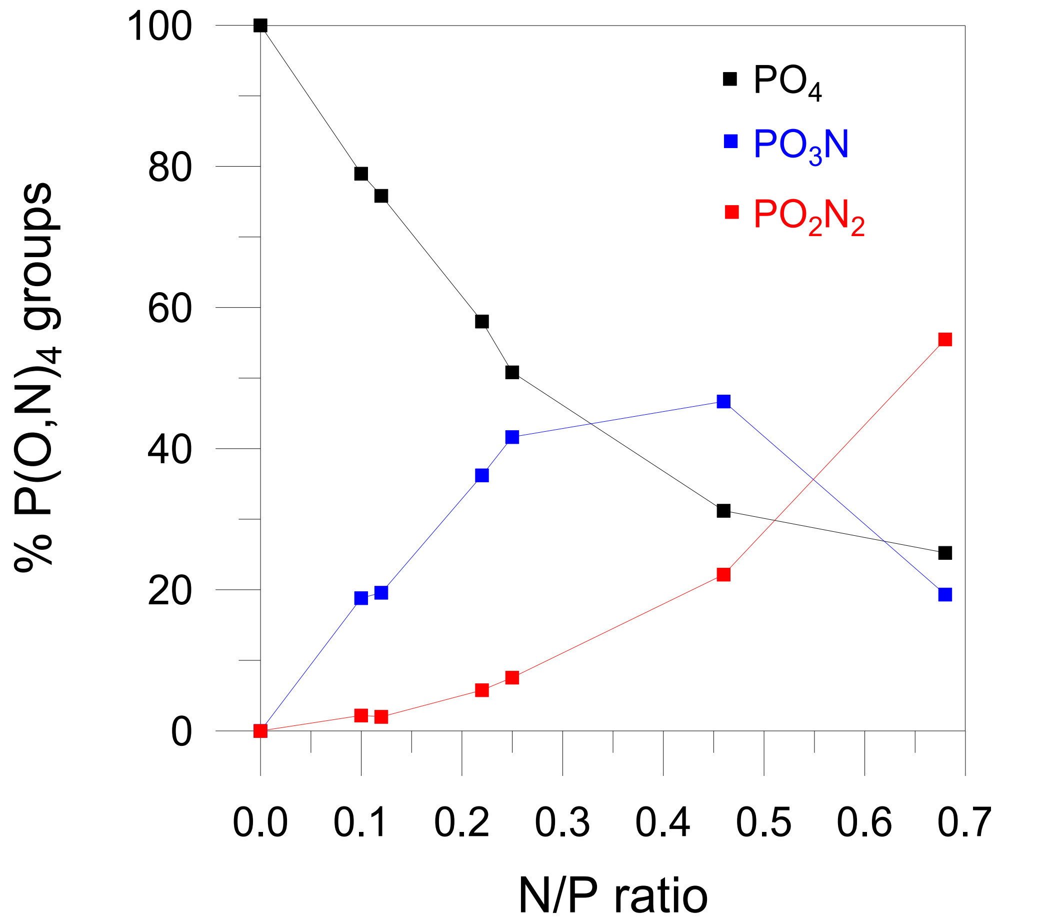
-300 ppm: NSi_3

Si–N<(Si)(Si)

Structure of oxynitride glasses



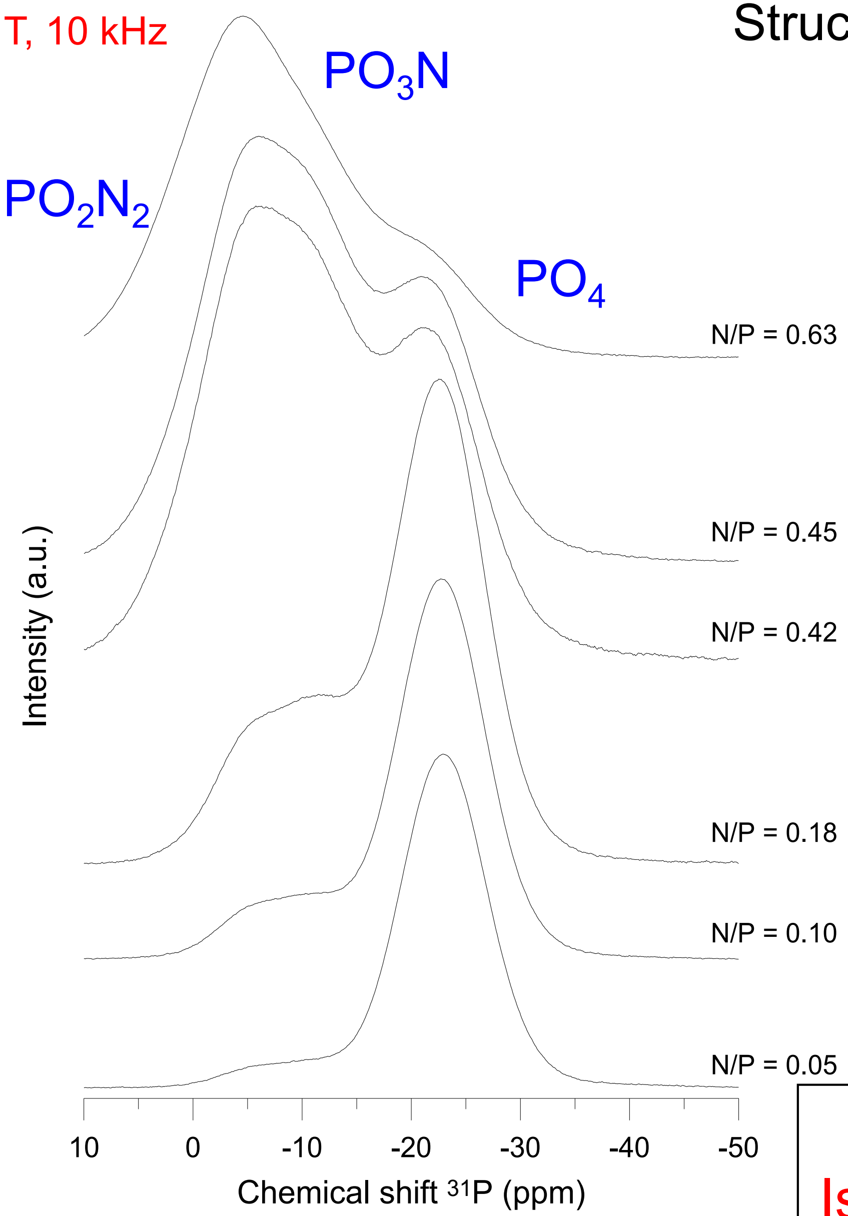
Structural groups distribution in $\mathbf{NaPO_{3-3x/2}N_x}$ glasses



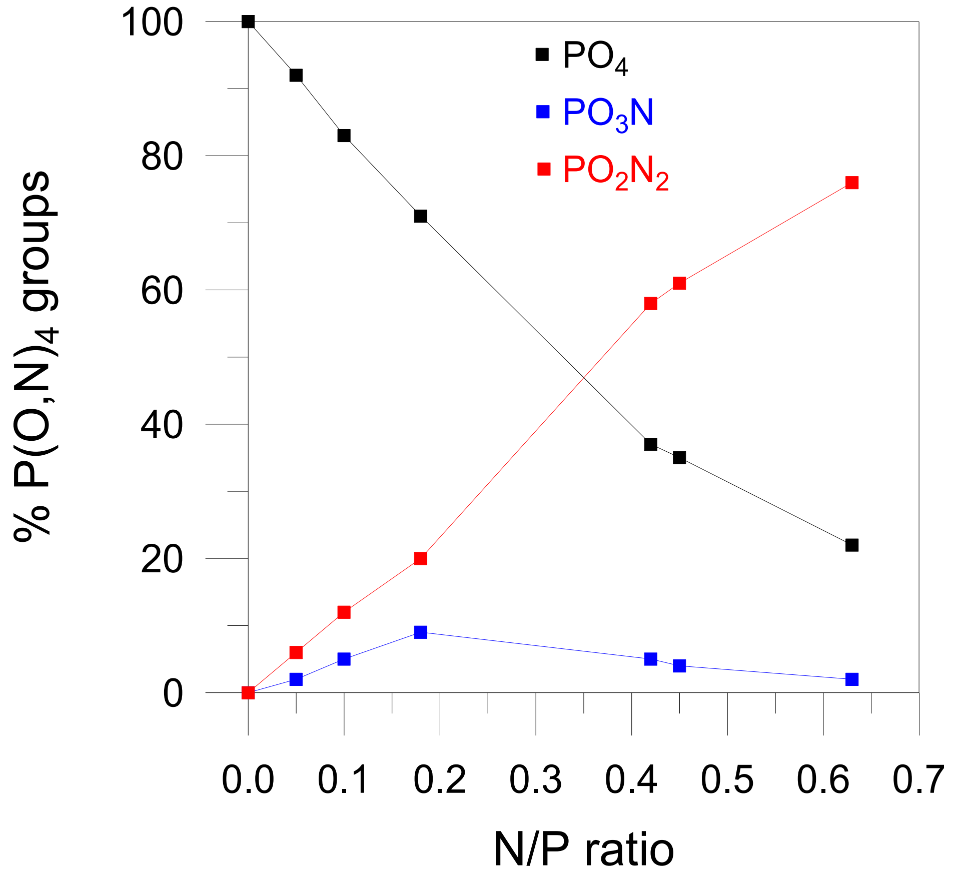
1. PO_3N formed
2. PO_2N_2 from PO_3N-PO_4 regions

Structure of oxynitride glasses

^{31}P MAS NMR
9.4 T, 10 kHz

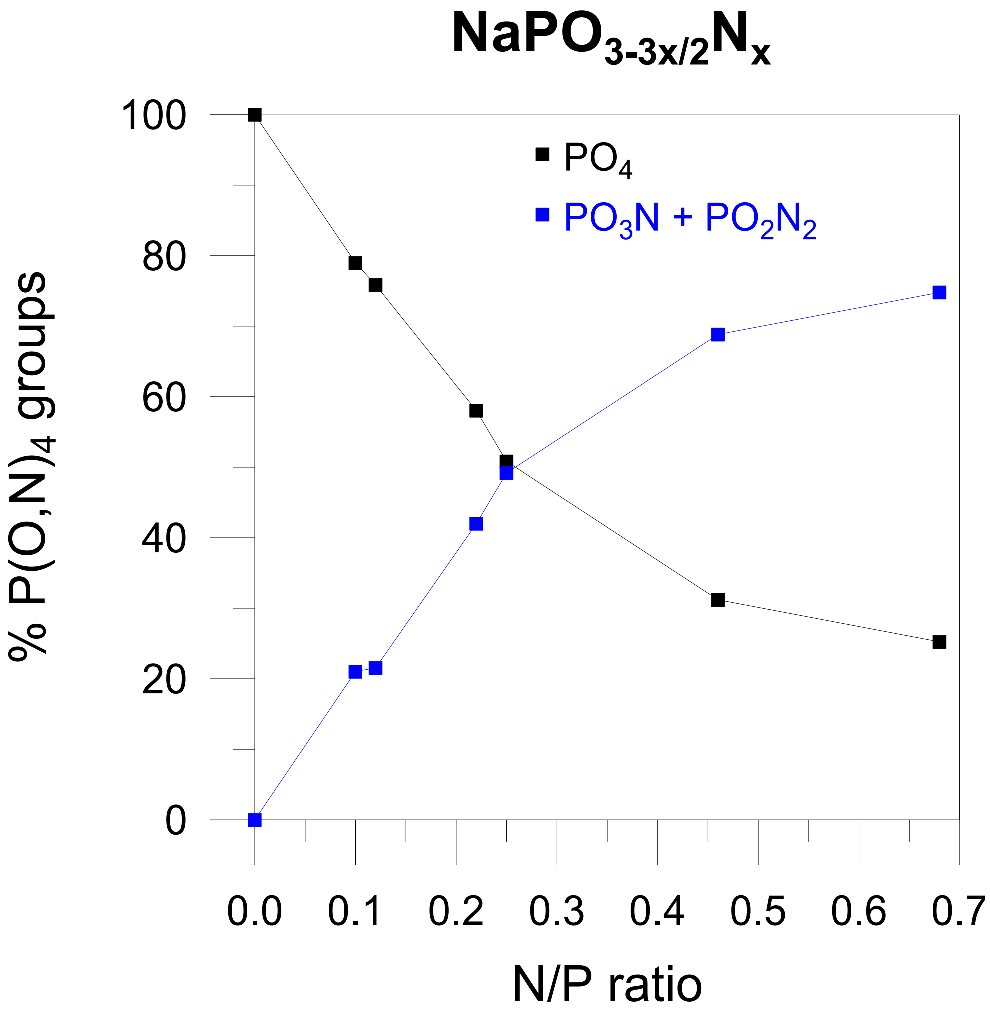


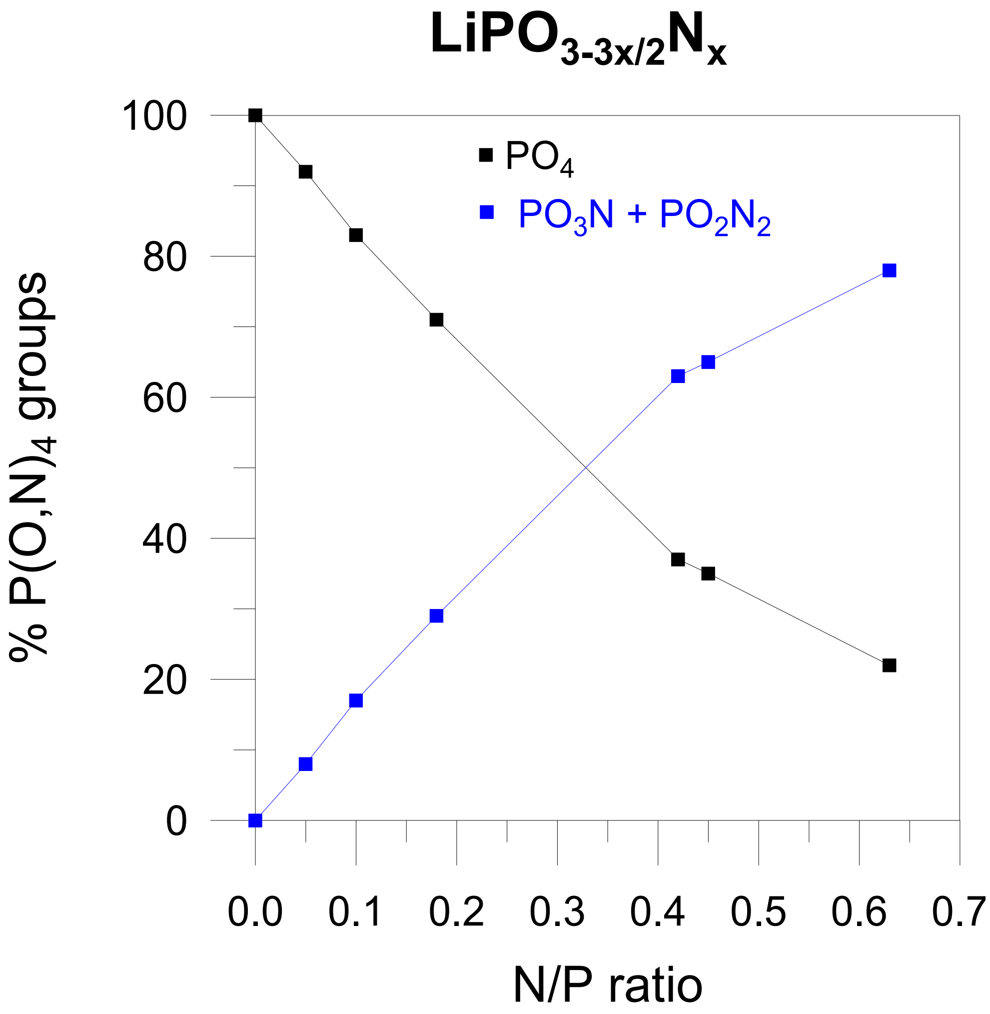
Structural groups distribution in $\mathbf{LiPO_{3-3x/2}N_x}$ glasses



Much lower content of PO_3N groups
Is nitrogen segregated in regions of PO_2N_2 ?

Structure of oxynitride glasses



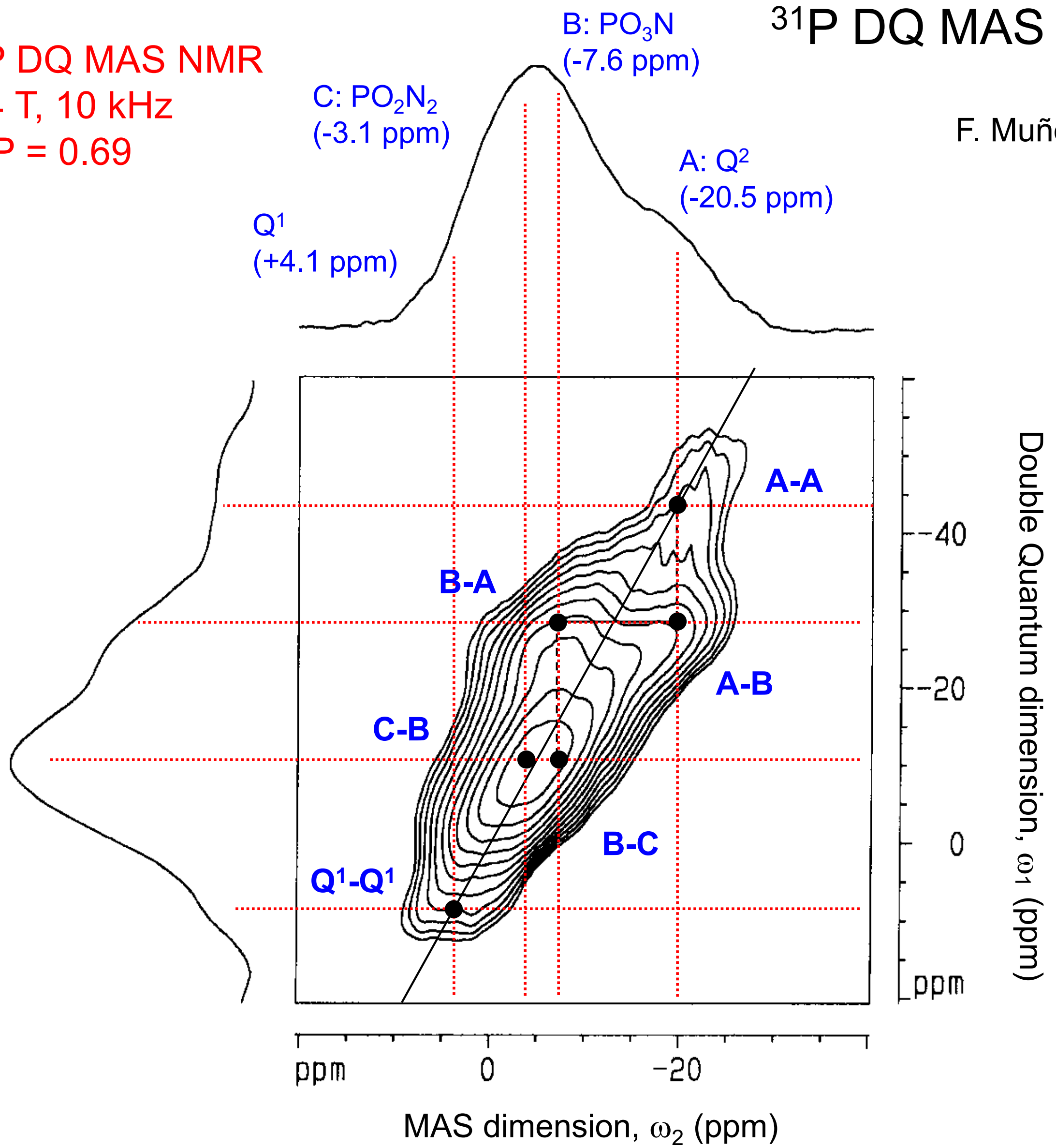


Structure of oxynitride glasses

^{31}P DQ MAS NMR
9.4 T, 10 kHz
N/P = 0.69

^{31}P DQ MAS NMR in $\mathbf{Li_{0.25}Na_{0.25}Pb_{0.25}PO_{3-3x/2}N_x}$

F. Muñoz *et al.*, J. Non-Cryst. Solids 324 (2003) 142-149



Correlations

PO_4-PO_4

PO_4-PO_3N

PO_3N-PO_2N_2

Q^1-Q^1 (Pyrophosphate)

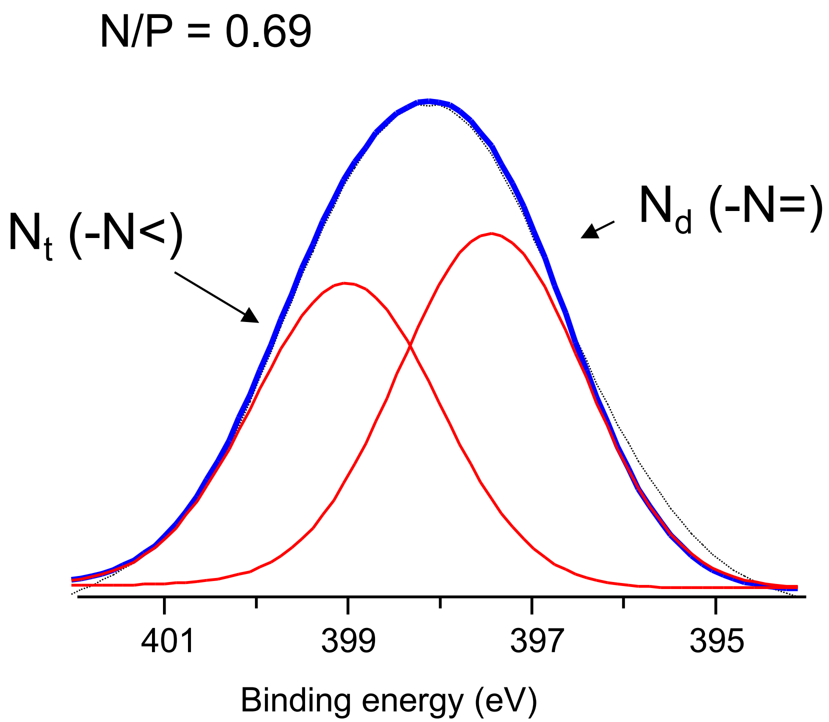
Homogeneous distribution of oxynitride microdomains

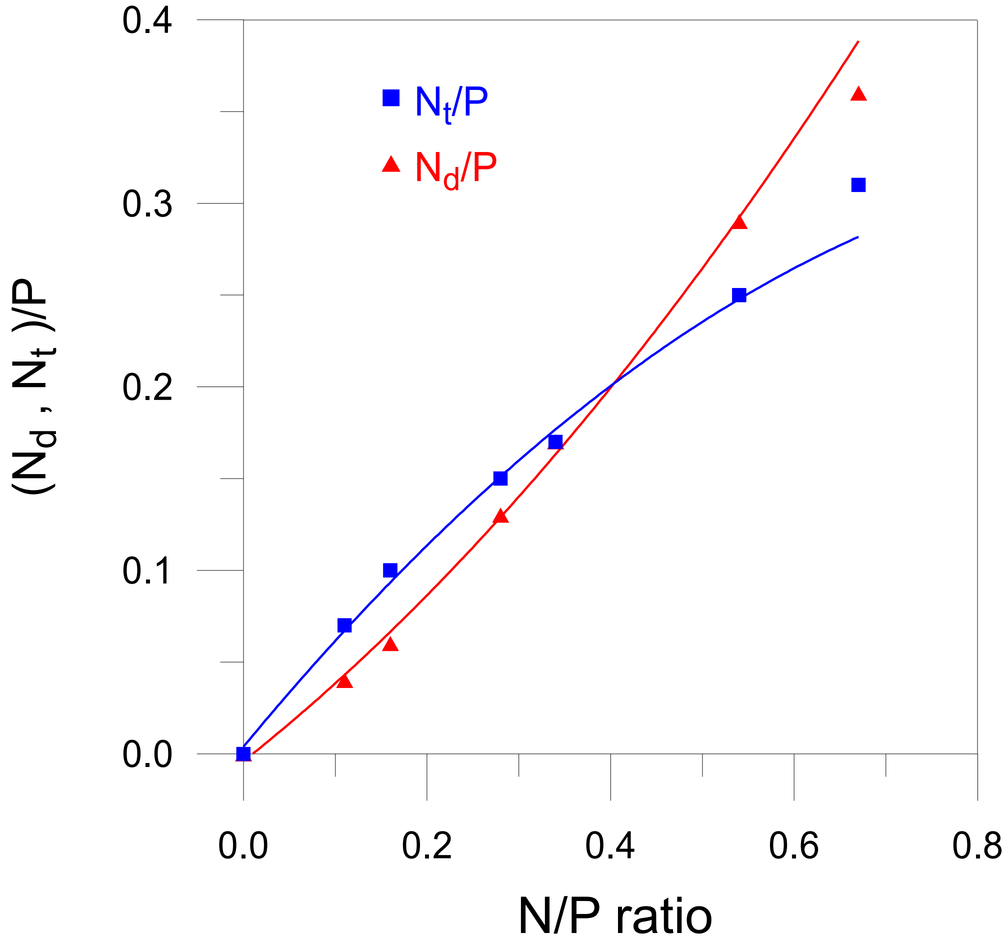
Structure of oxynitride glasses

N_{1s} XPS

Intensity (a.u.)

XPS of **$Li_{0.25}Na_{0.25}Pb_{0.25}PO_{3-3x/2}N_x$** glasses

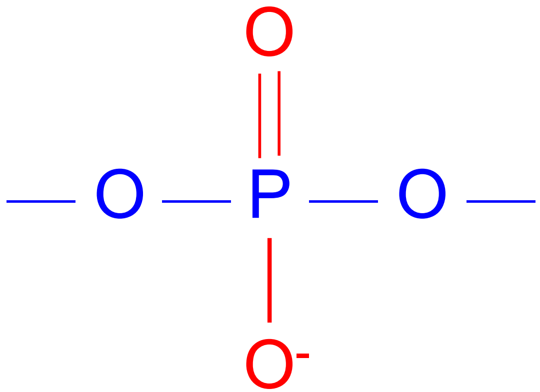




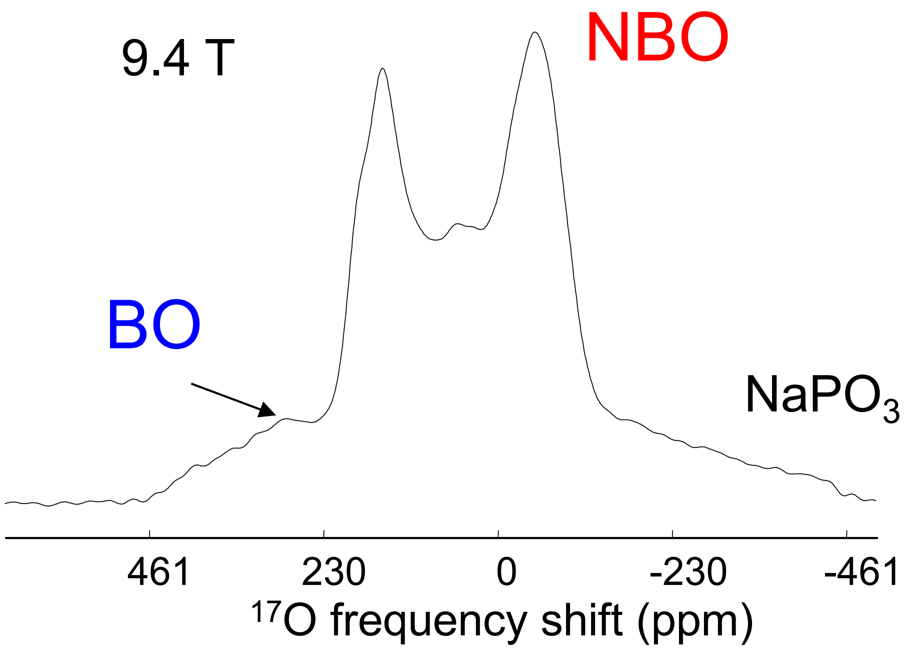
F. Muñoz *et al.*, J. Non-Cryst. Solids 324 (2003) 142-149

Structure of oxynitride glasses

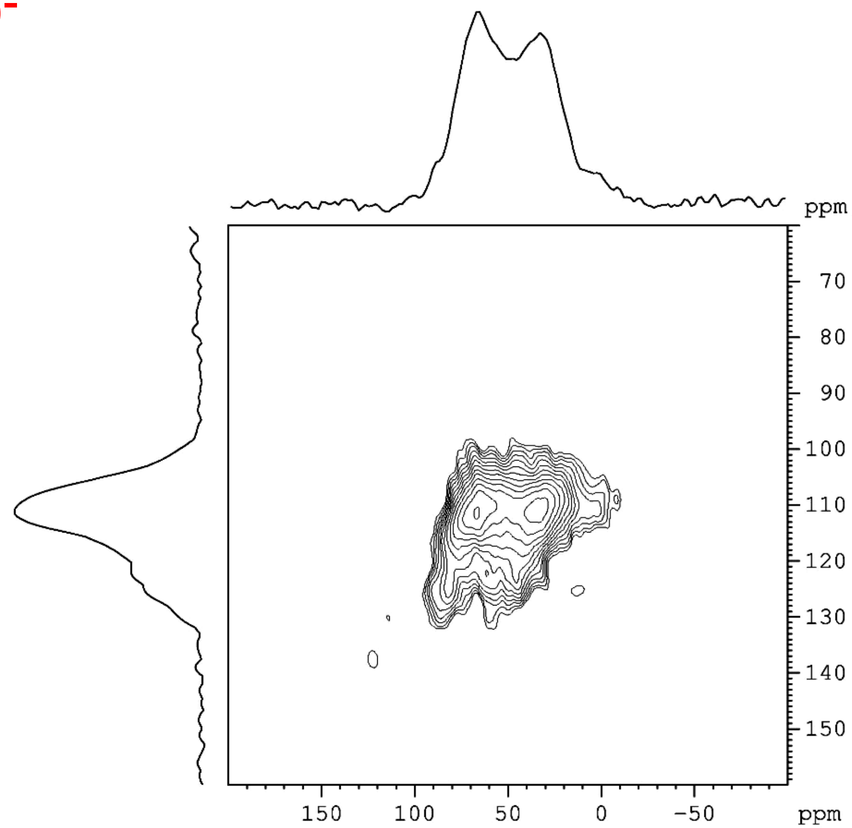
In a metaphosphate glass:



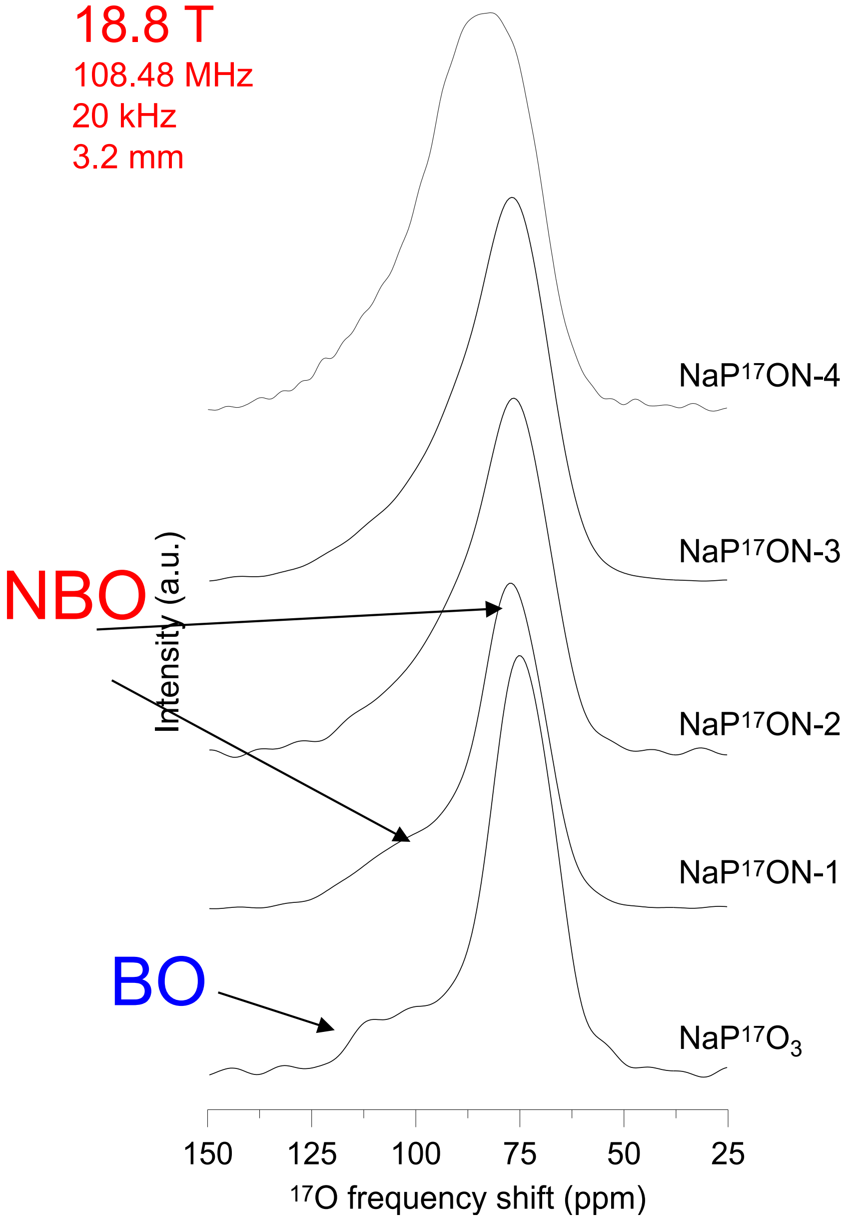
^{17}O NMR
9.4 T

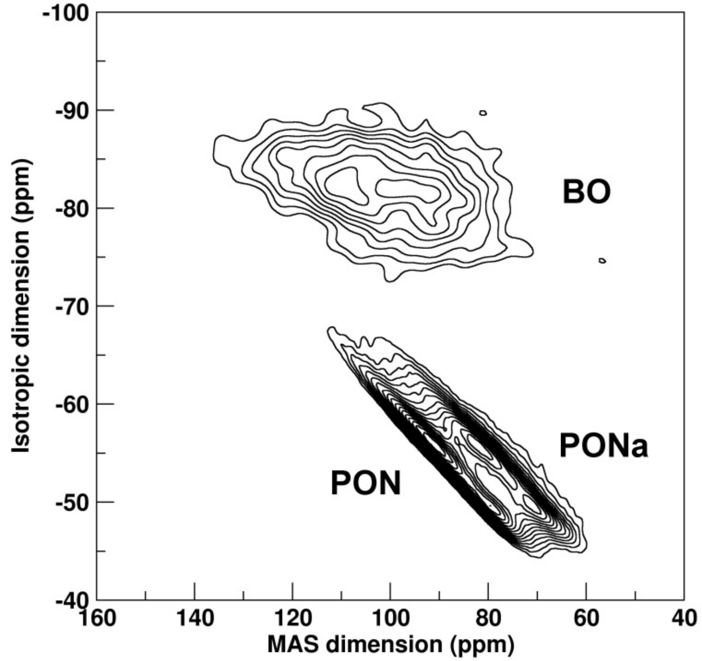


3QMAS ^{17}O
9.4 T

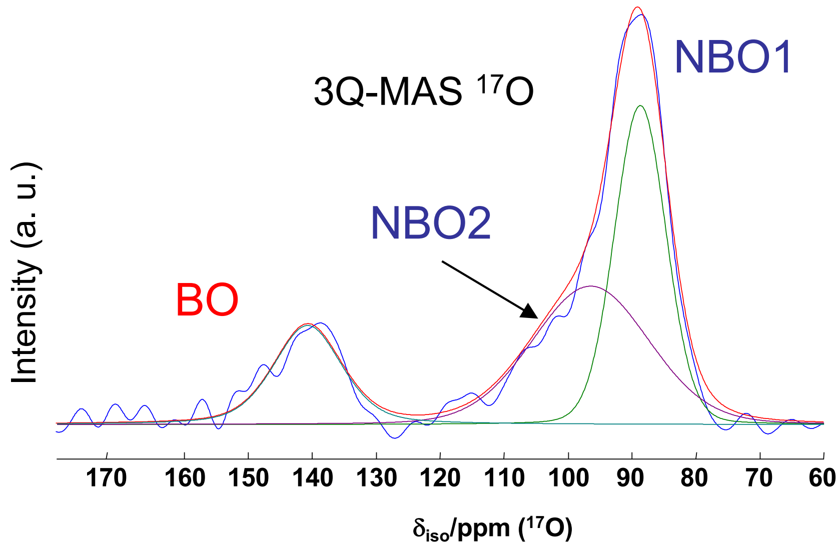


Structure of oxynitride glasses



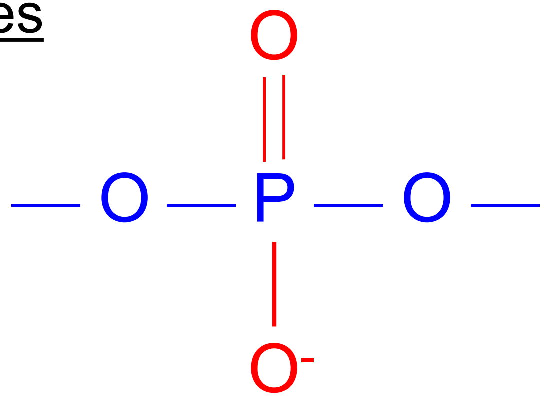


Down-field shift of ^{17}O resonance in PON of imidophosphates (J. Am. Chem. Soc. 105 (1983) 6475)

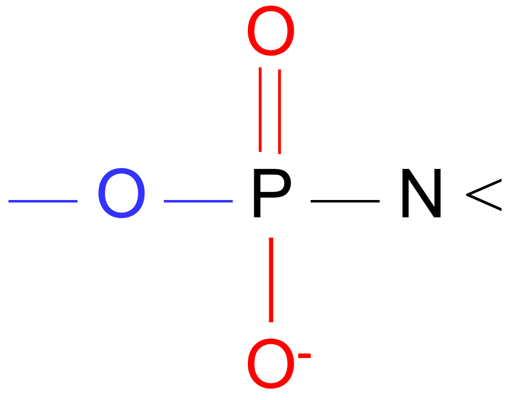


Structure of oxynitride glasses

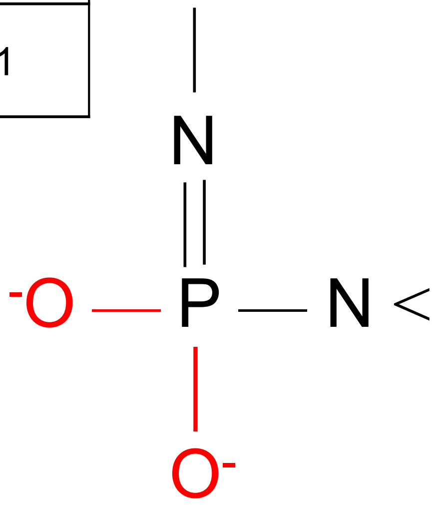
Sample	δ_{CS}	% PON
$NaP^{17}ON$	8.0 (4.0)	0
$NaP^{17}ON$-1	14.9 (5.2)	20
$NaP^{17}ON$-2	14.2 (7.1)	41
$NaP^{17}ON$-3	12.2 (8.3)	53
$NaP^{17}ON$-4	15.8 (8.8)	81



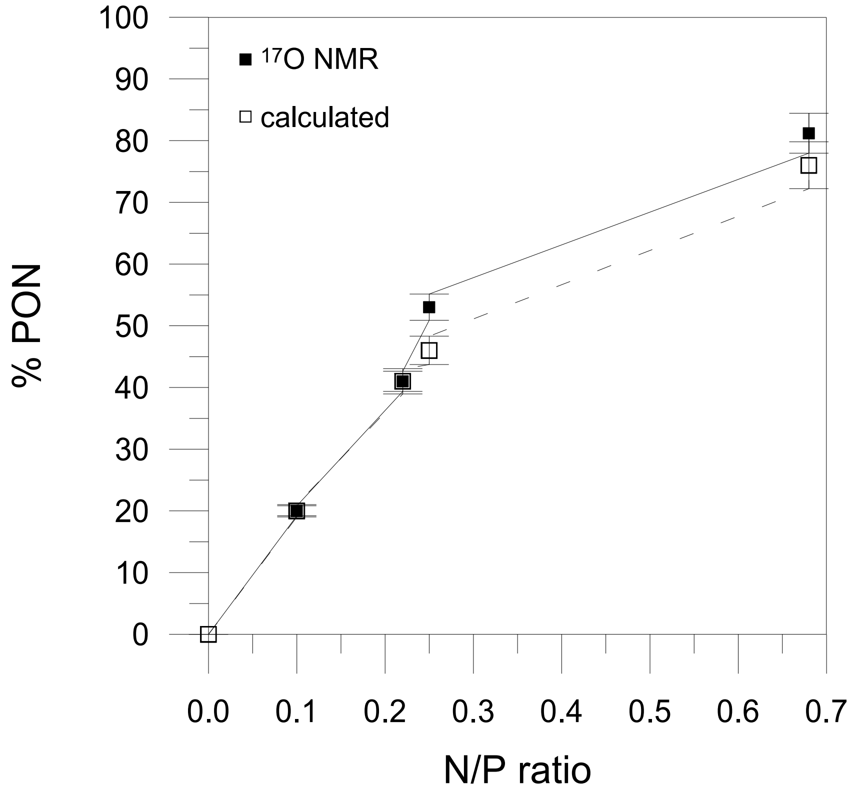
PO_4: BO/NBO = 0.5



PO_3N: BO/NBO = 0.25



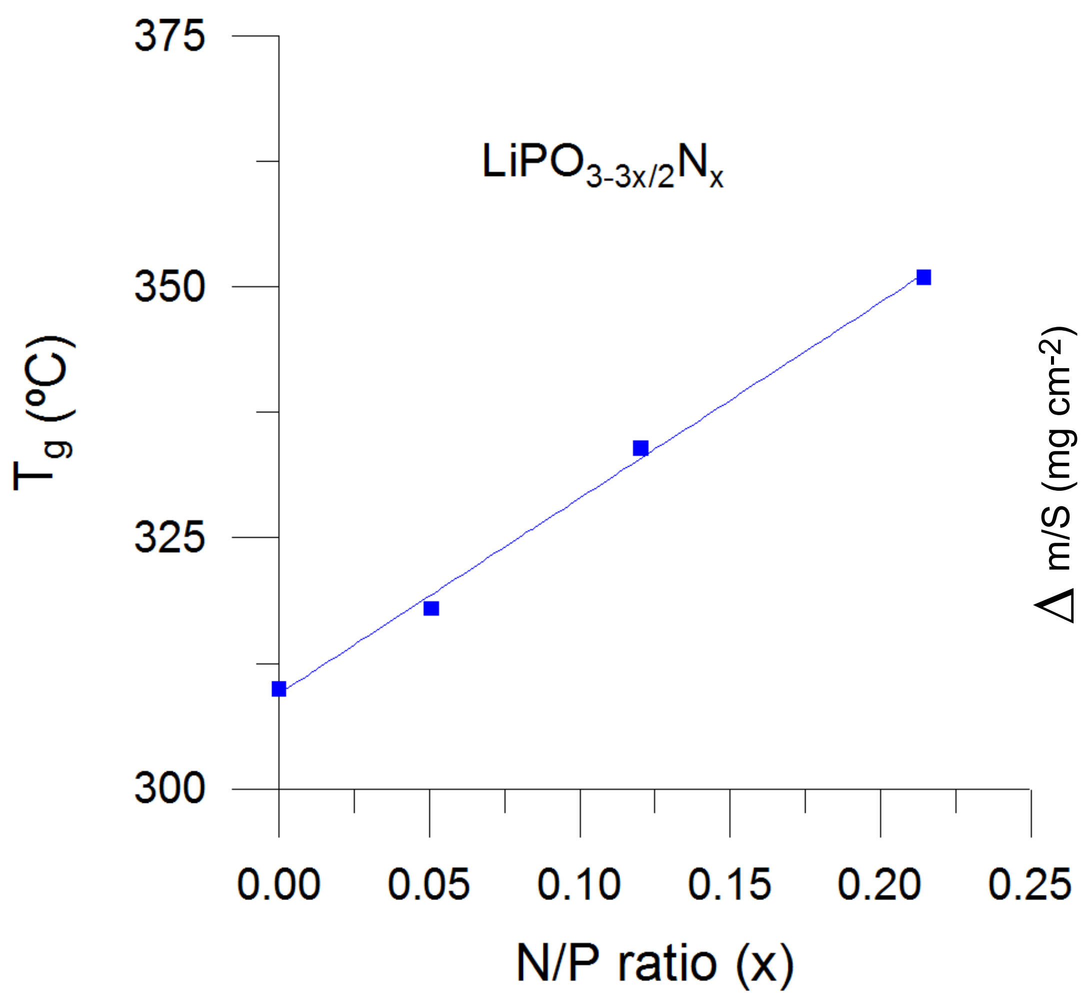
PO_2N_2: BO/NBO = 0

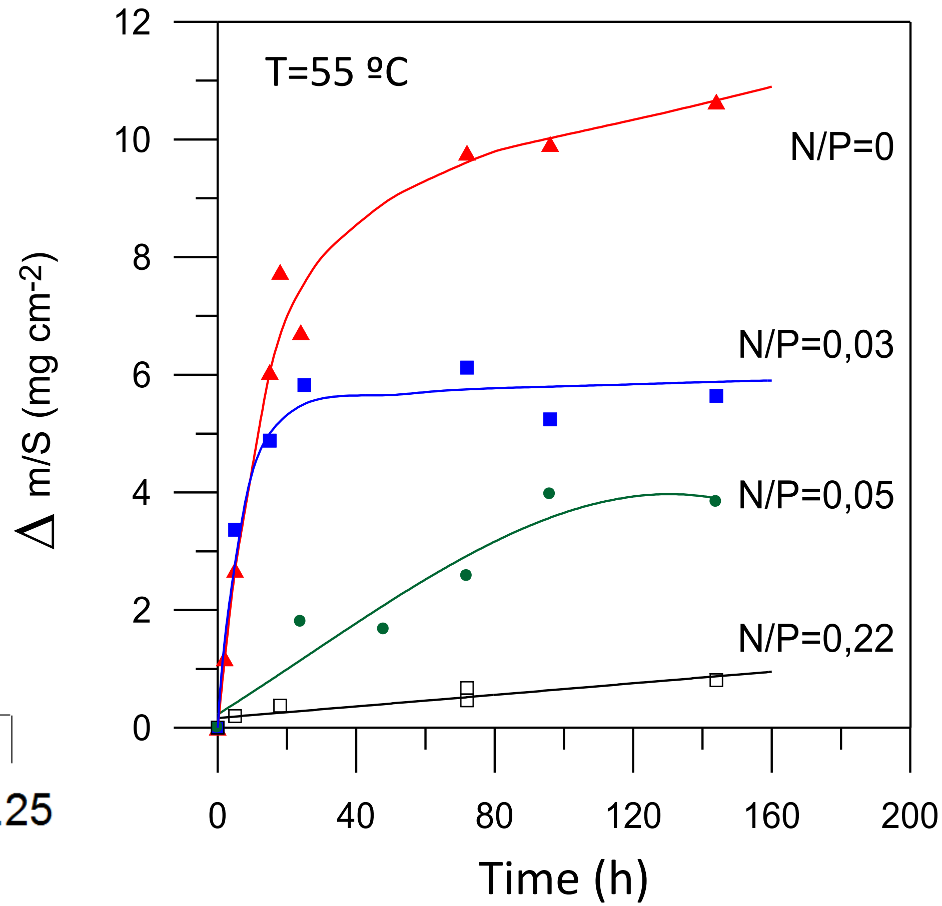


$$\% \text{ PON} = [100\cdot(x_{PO3N} + x_{PO2N2})]/[x_{PO4} + x_{PO3N} + x_{PO2N2}]$$

Properties and applications

Oxynitride phosphate glasses: thermal and chemical stability

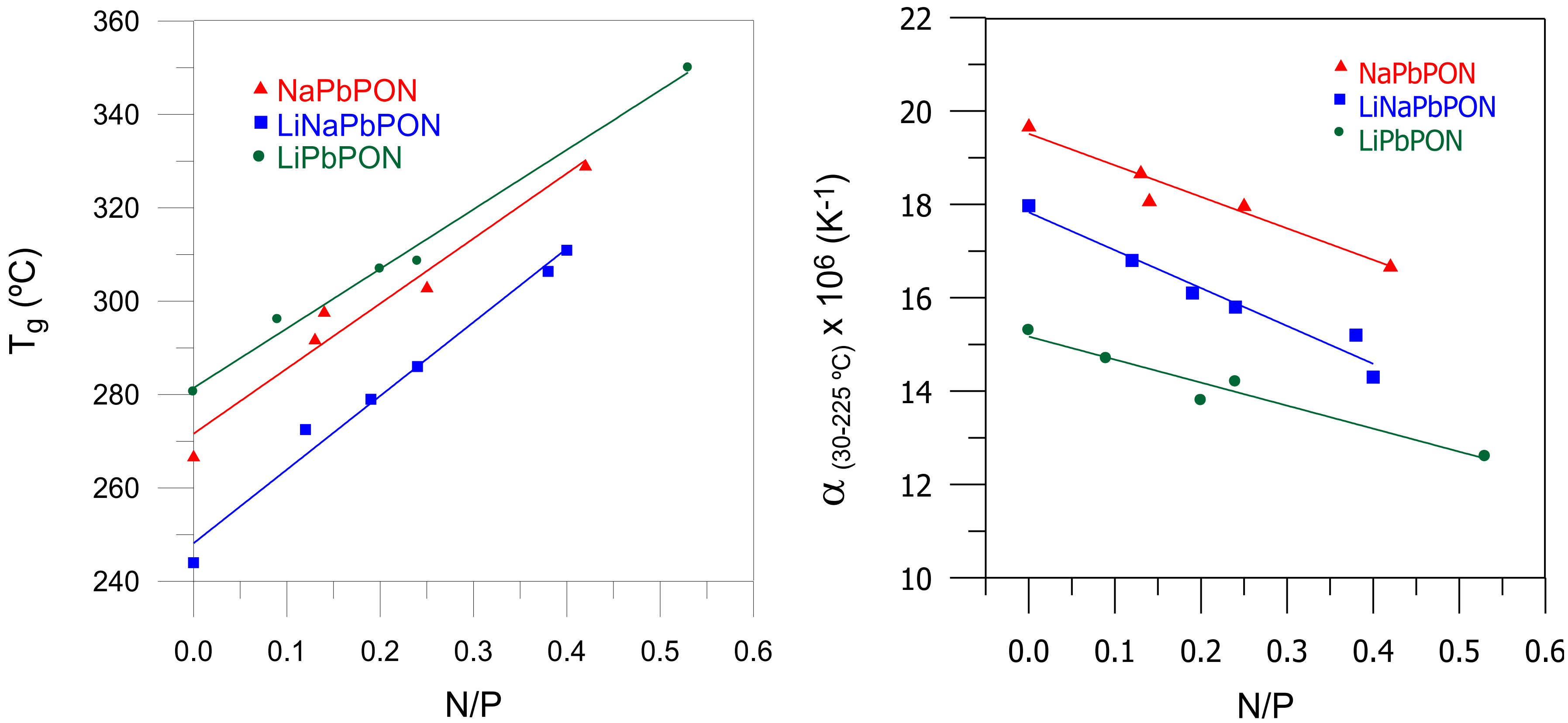




Weight loss *vs* time at 55ºC
In LiNaPbPON glasses

Low temperature sealing glasses

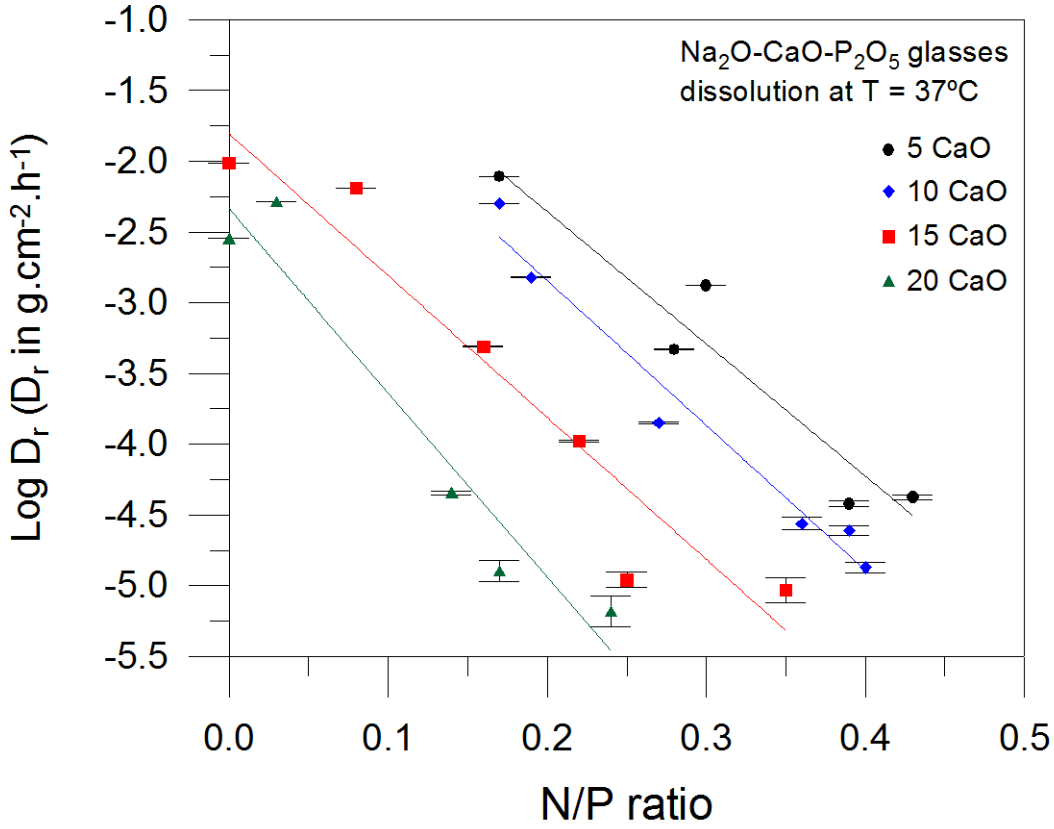
Properties of Li_2O-Na_2O-PbO-P_2O_5 sealing glasses



F. Muñoz et al, Phys. Chem. Glasses 43C (2002) 39

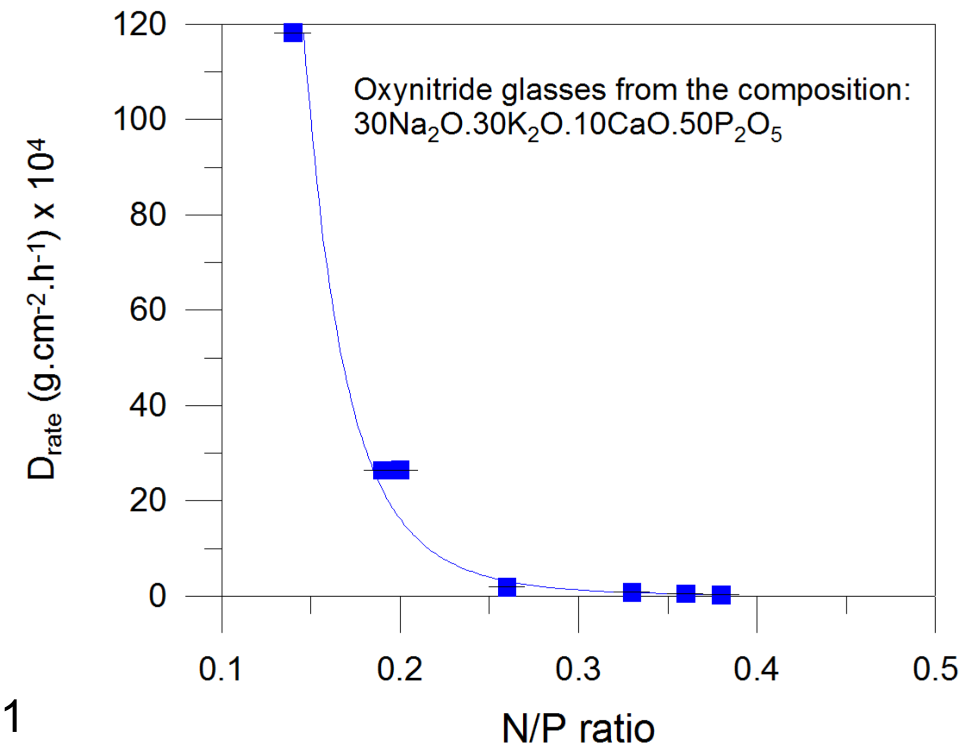
Nitrogen variable content allows for the adjustment of the softening temperatures as well as the coefficients of thermal expansion

Biocompatible/resorbable materials



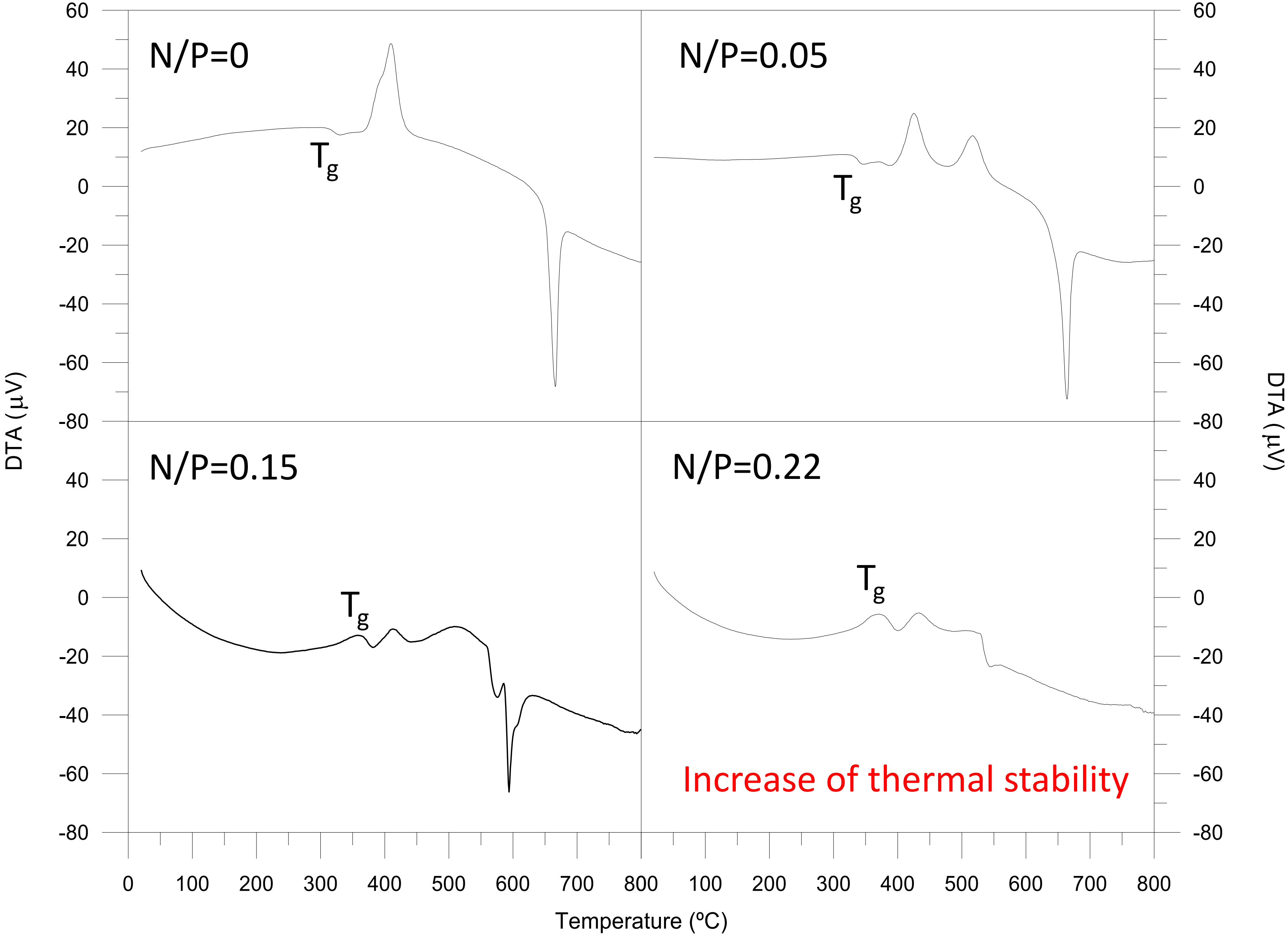
Control of the dissolution rate:

- CaO/Na_2O ratio
- Content of nitrogen in the glass



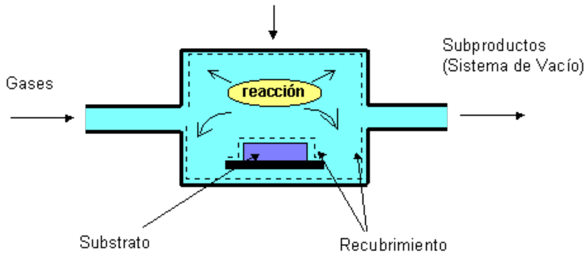
Q. Riguidel *et al.* Acta Biomaterialia 7 (2011) 2631

Oxynitride phosphate glasses: stability against crystallization in LiPON



Solid electrolytes for lithium batteries

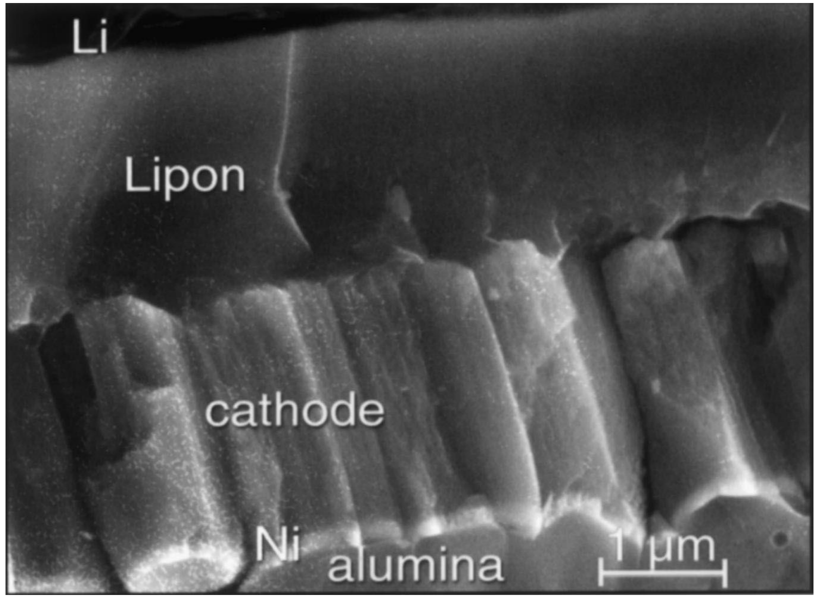
RF magnetron sputtering



Li_3PO_4 → *LiPON* $(Li_{\sim 2.8}PO_{\sim 3.5}N_x)$ amorphous ← N_2

σ (25ºC) ~ $2 \cdot 10^{-6}$ S cm^{-1}, E_a = 0.55 eV

Yu *et al.*, *J. Electrochem Soc.* 144(2) (1997) 524



Bates *et al.*, *Solid State Ionics* 135 (2000) 33

„I learned that adding nitrogen to sodium metaphosphate glasses improves their durability in contact with air and water vapor. So we decided to sputter the lithium orthophosphate in nitrogen rather than the standard gas mixture of argon and oxygen. … the presence of this small amount of nitrogen greatly improves the performance of the electrolyte.“

J. B. Bates

Development of phosphate and oxynitride phosphate glasses

Solid electrolytes for lithium batteries

Wang *et al.*, *J. Non-Cryst. Solids*, 183 (1995) 297-306

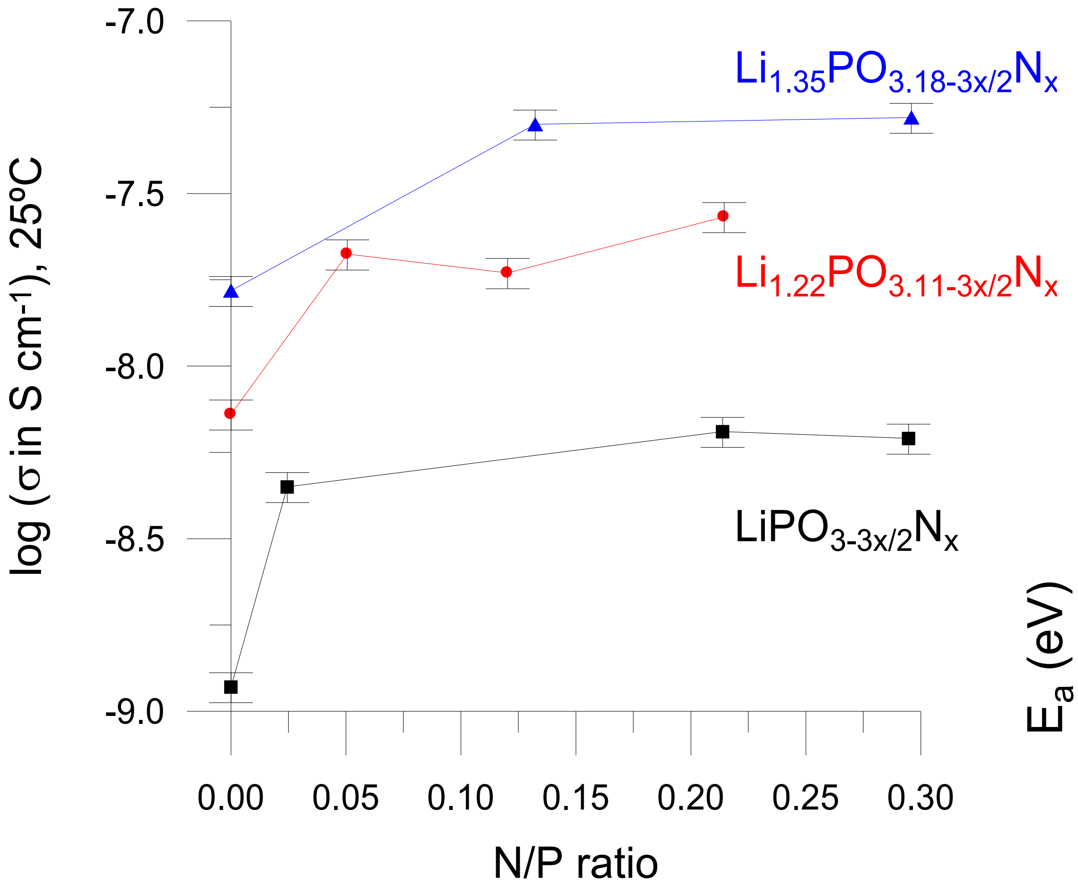
Table 4
Conductivity data of lithium phosphorus oxynitride glasses

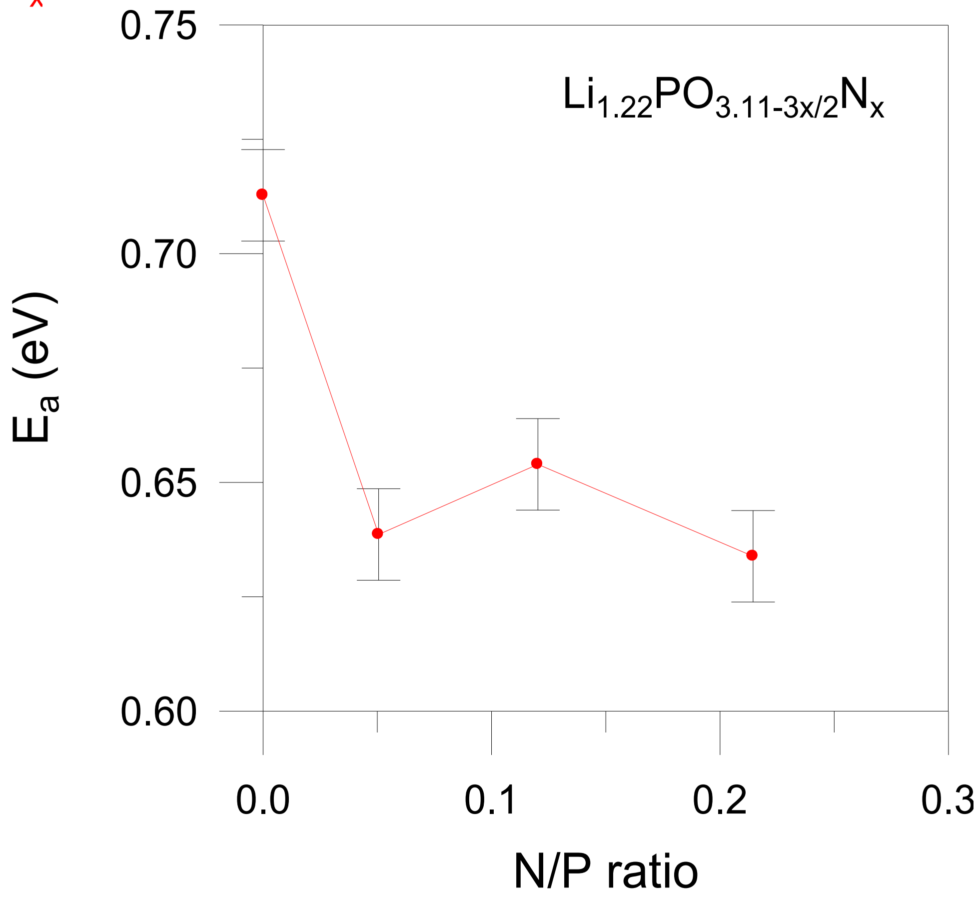
Sample	$\sigma_{25°C}$ (S cm^{-1})	E_a (eV)	σ_0 (S cm^{-1} K)
$Li_{0.92}PO_{2.96}$ [a]	2.5×10^{-9}	0.74 ± 0.01	$2.3 \times 10^6 \pm 1.1$
$Li_{0.86}PO_{2.84}N_{0.06}$ [b]	5.4×10^{-9}	0.70 ± 0.01	$9.3 \times 10^5 \pm 2.7$
$Li_{0.88}PO_{2.31}N_{0.42}$ [b]	1.7×10^{-8}	0.67 ± 0.01	$1.2 \times 10^6 \pm 1.5$
$Li_{1.28}PO_{3.14}$ [a]	4.6×10^{-8}	0.65 ± 0.01	$1.1 \times 10^6 \pm 1.3$
$Li_{0.93}PO_{2.82}N_{0.10}$ [a]	1.1×10^{-7}	0.60 ± 0.01	$4.7 \times 10^5 \pm 1.2$
$Li_{0.99}PO_{2.55}N_{0.30}$ [a]	3.0×10^{-7}	0.60 ± 0.01	$1.2 \times 10^6 \pm 1.3$
$Li_{1.24}PO_{2.24}N_{0.58}$ [a,c]	3.6×10^{-7}	0.58 ± 0.01	$8.0 \times 10^5 \pm 2.5$
$Li_{1.41}PO_{2.41}N_{0.53}$ [a,c]	3.7×10^{-7}	0.57 ± 0.01	$5.3 \times 10^5 \pm 1.3$

[a] Single-phase impedance spectrum. [b] Phase-separated impedance spectrum. [c] Sample prepared and chemically analyzed by Boukbir and Marchand [7].

- Higher σ in the glassy material than in the crystalline counterpart
- Increase in σ with increasing nitrogen content
- Increase in the thermal and mechanical stability of the electrolyte
- The oxynitride may act as a protecting barrier for Li-metal

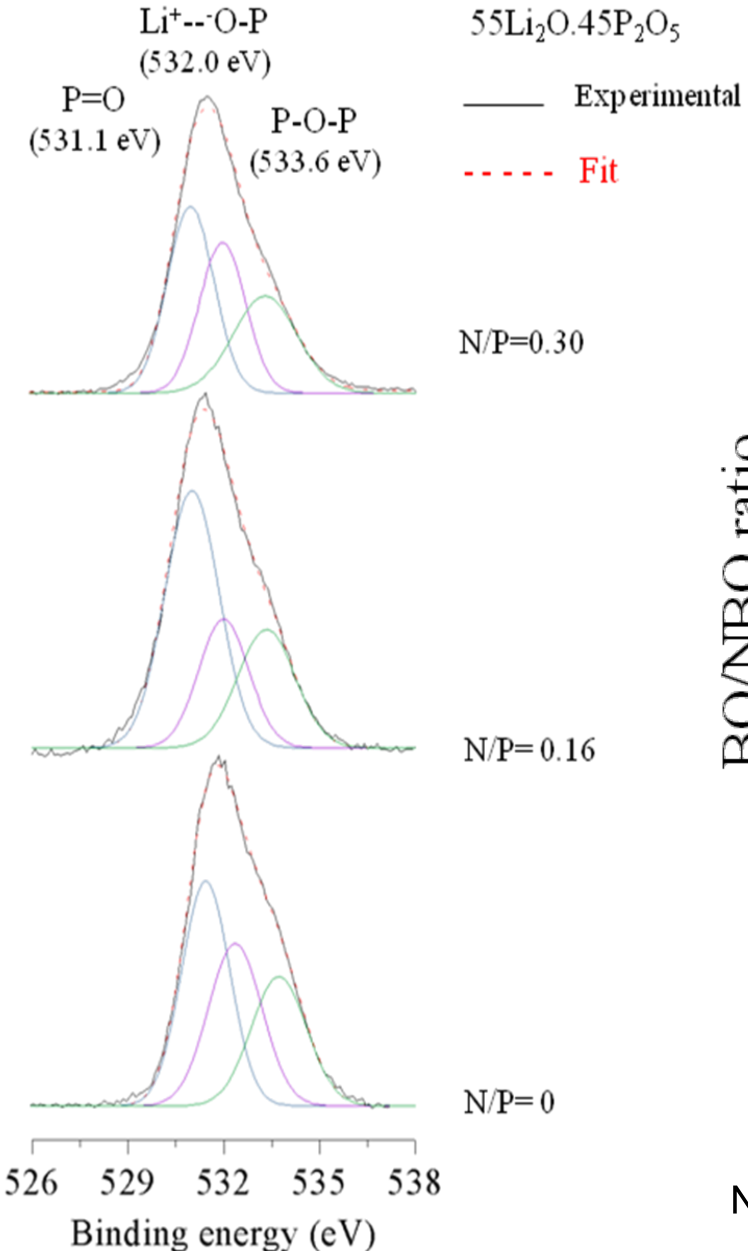
Solid electrolytes for lithium batteries

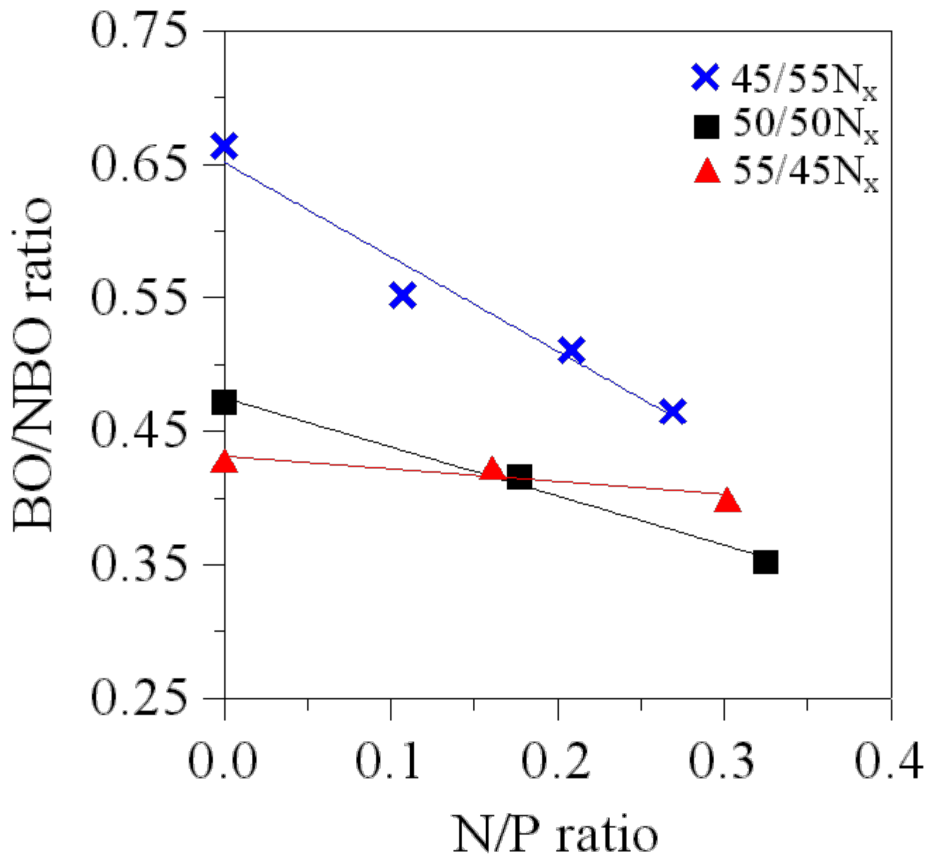




Solid electrolytes for lithium batteries

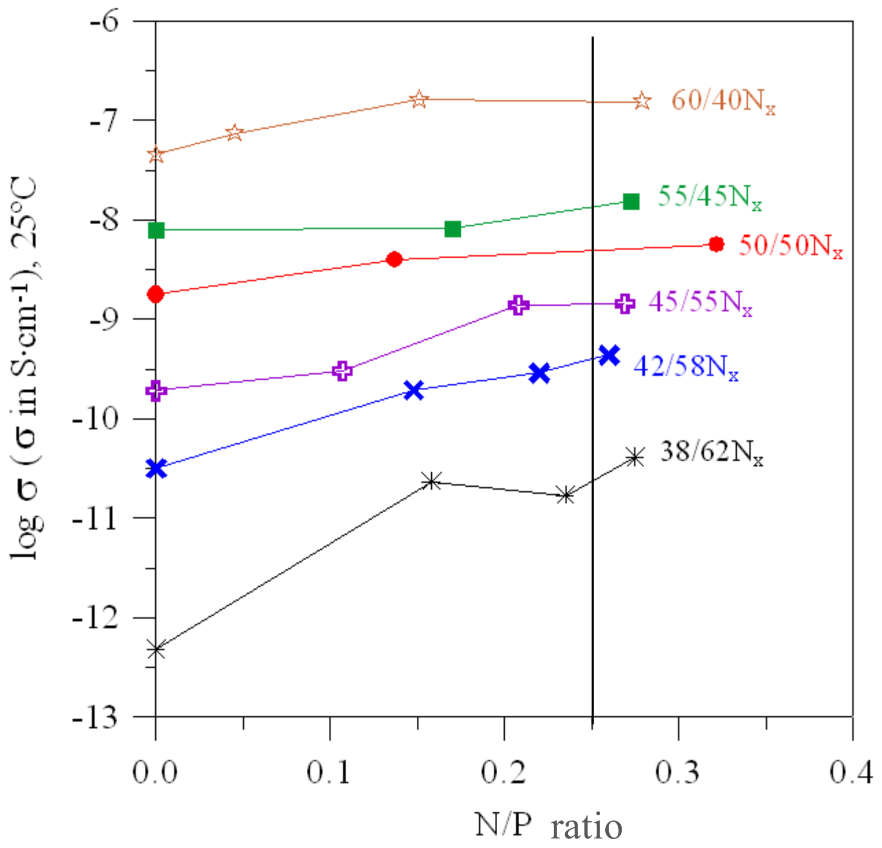
XPS O_{1s}

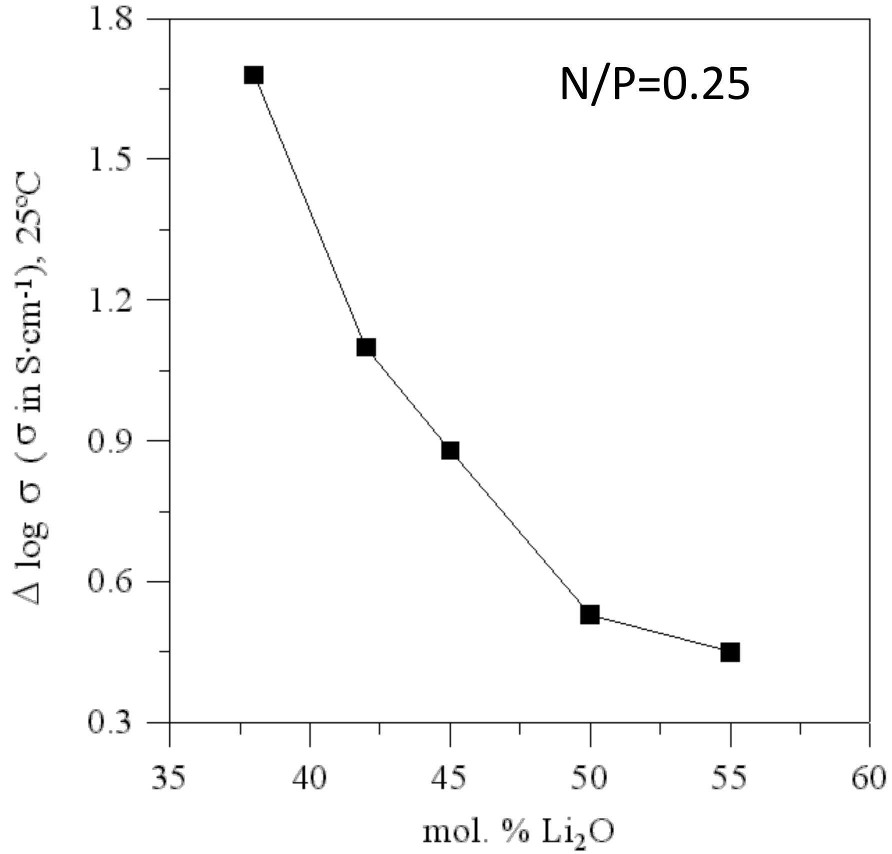




N. Mascaraque *et al.* Solid State Ionics 233 (2013) 73-79

Solid electrolytes for lithium batteries





The change in BO/NBO ratio after nitridation decreases wtih Li_2O

The higher the BO/NBO change, the higher the increase in σ

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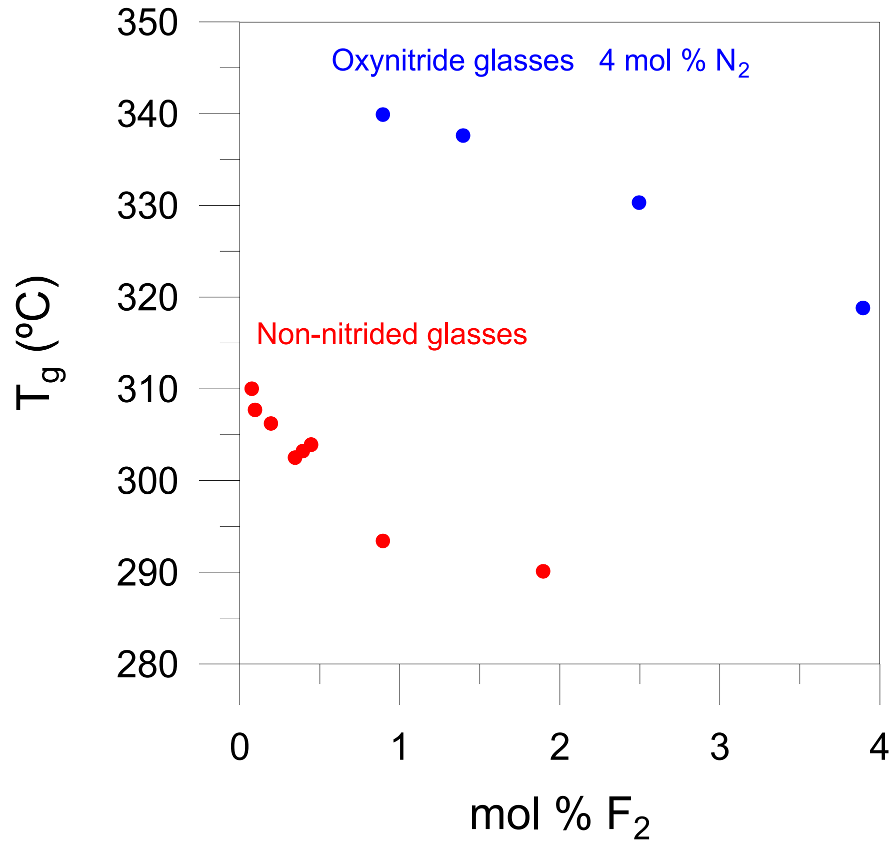
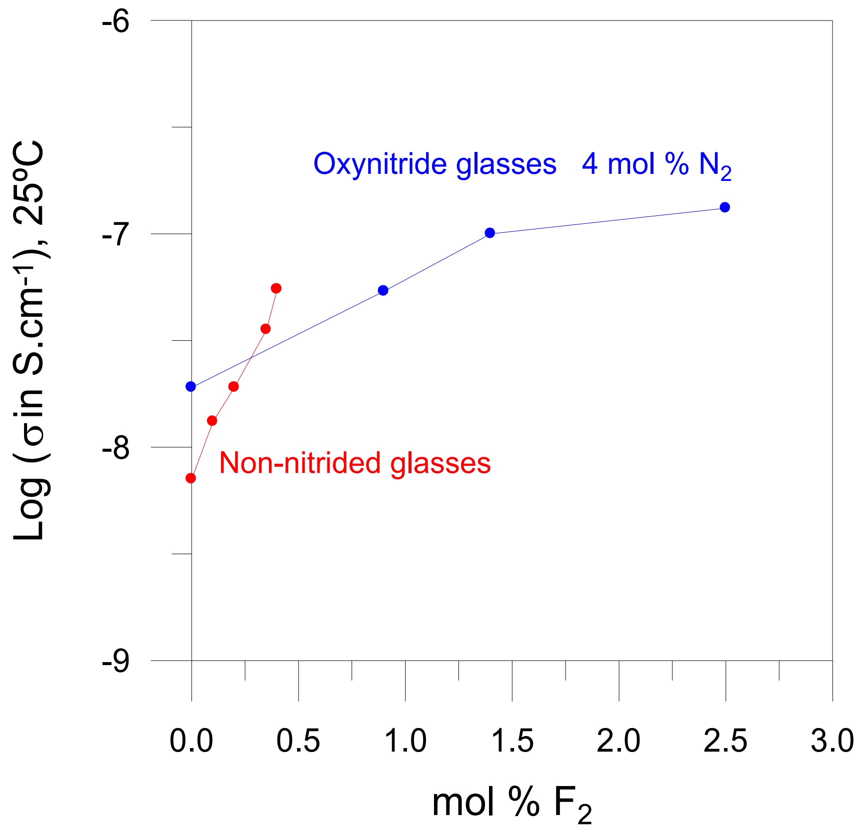
Solid electrolytes for lithium batteries

Synthesis of $(55-x/2)Li_2O.xLiF.(45-x/2)P_2O_5$ glasses

1st melting: $55Li_2O.45P_2O_5 + NH_3 \longrightarrow$ Li-P-O-N

2nd melting: Li-P-O-N + LiF $\xrightarrow{N_2}$ Li-P-O-F-N



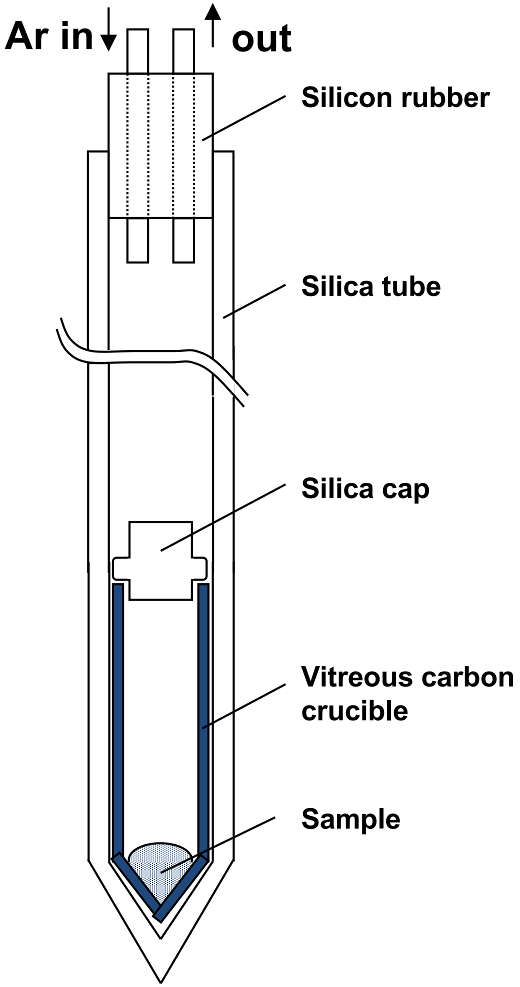


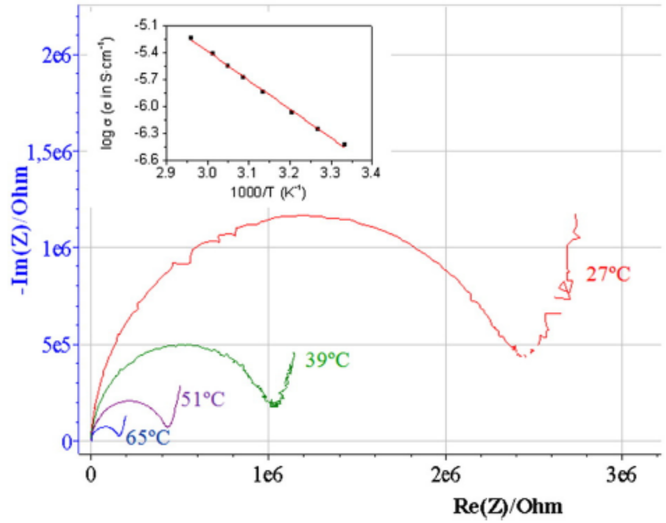
Mascaraque *et al.* Solid State Ionics 254 (2014) 40

Solid electrolytes for lithium batteries

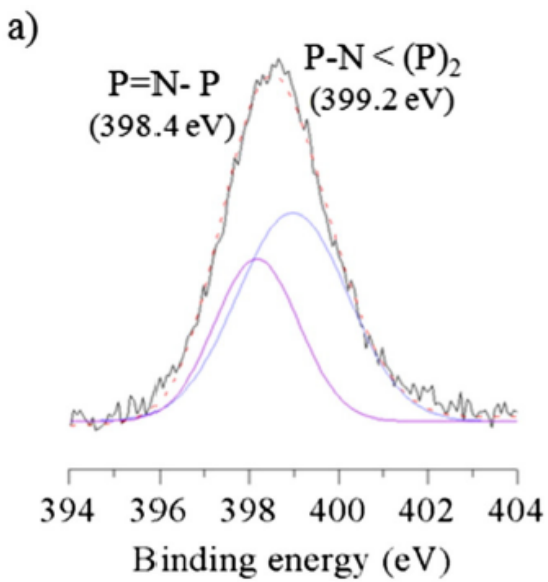
1 mol $Li_{1.22}PO_{2.66}N_{0.3}$ + 0.2 mol Li_2S

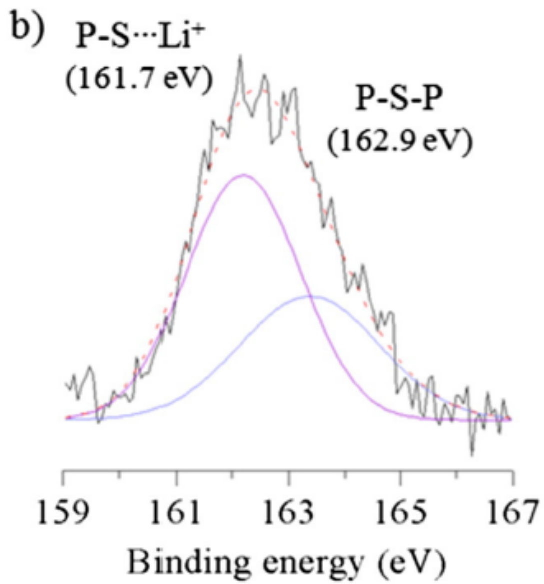
Melted @ 650ºC for 30 min in Ar flow using vitreous carbon crucible





Log σ LiPON = -7.8
Log σ LiPOSN = -6.6





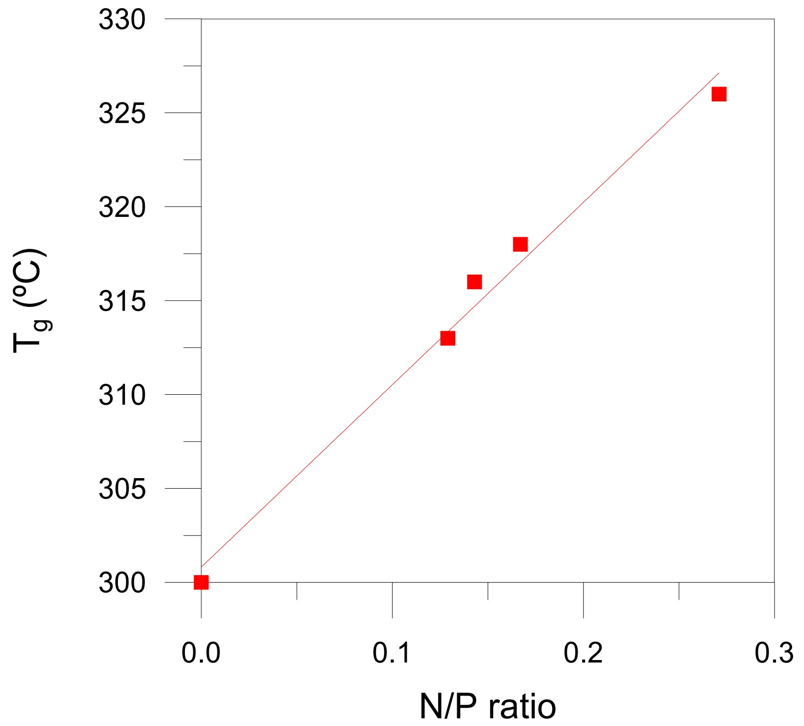
Mascaraque *et al.* J. Non-Cryst. Solids 405 (2014) 159

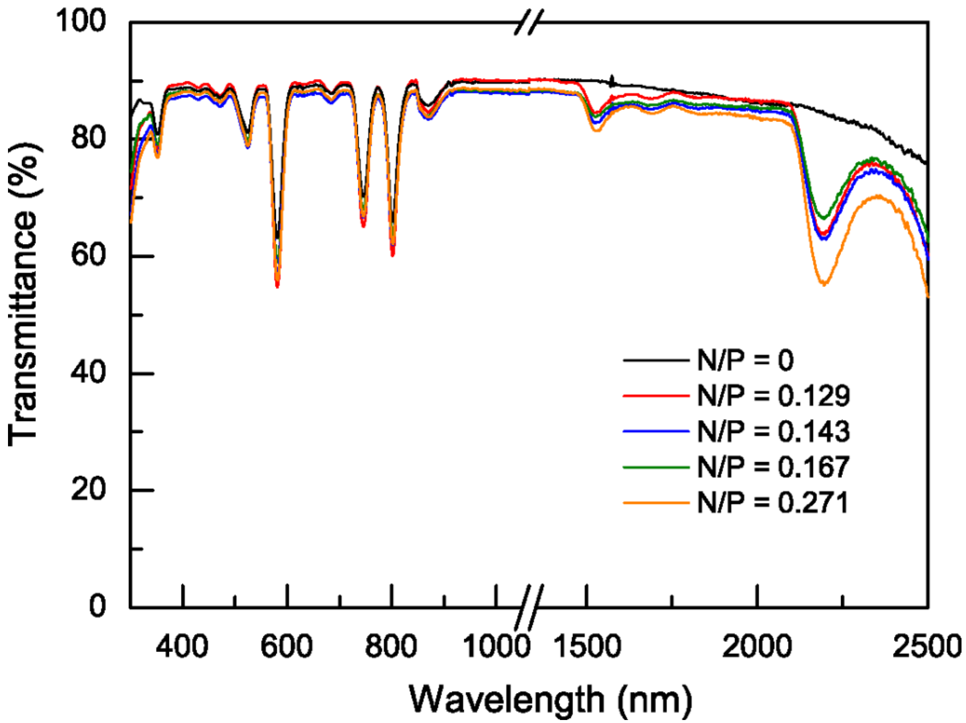
Nd-doped luminiscent oxynitride glasses

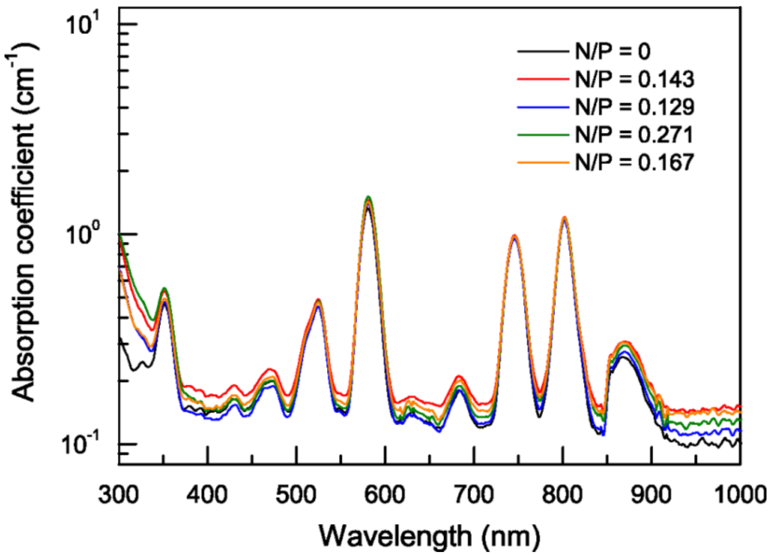
Optical properties of nitrided glasses

$15Na_2O\text{-}15K_2O\text{-}20BaO\text{-}50P_2O_5$
$+ 0.5$ wt. % Nd_2O_3

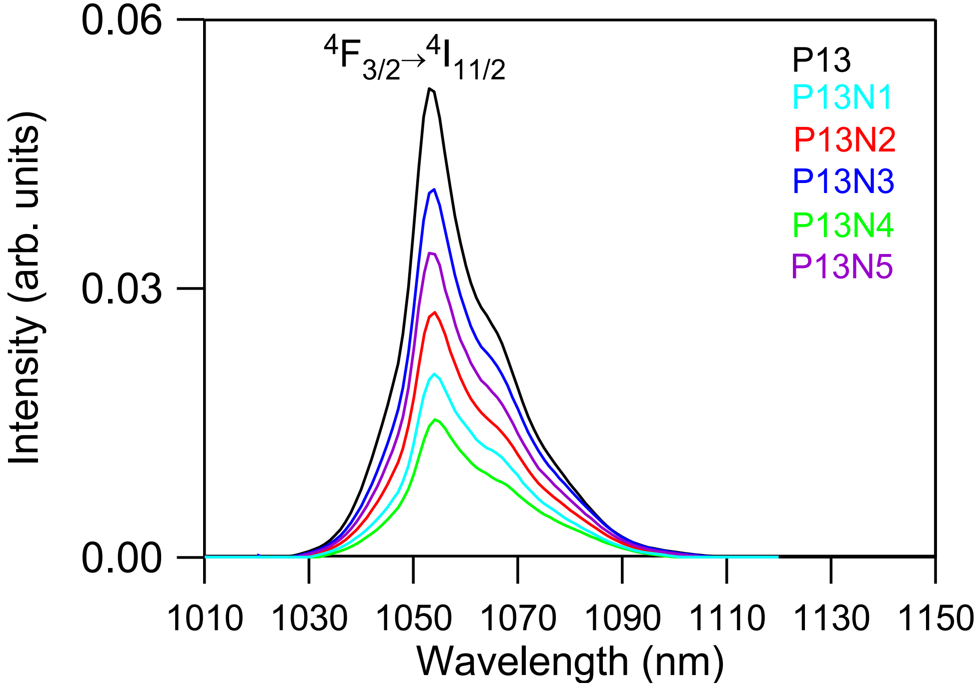
$Na_{0.3}K_{0.3}Ba_{0.2}PO_{3-3x/2}N_x$

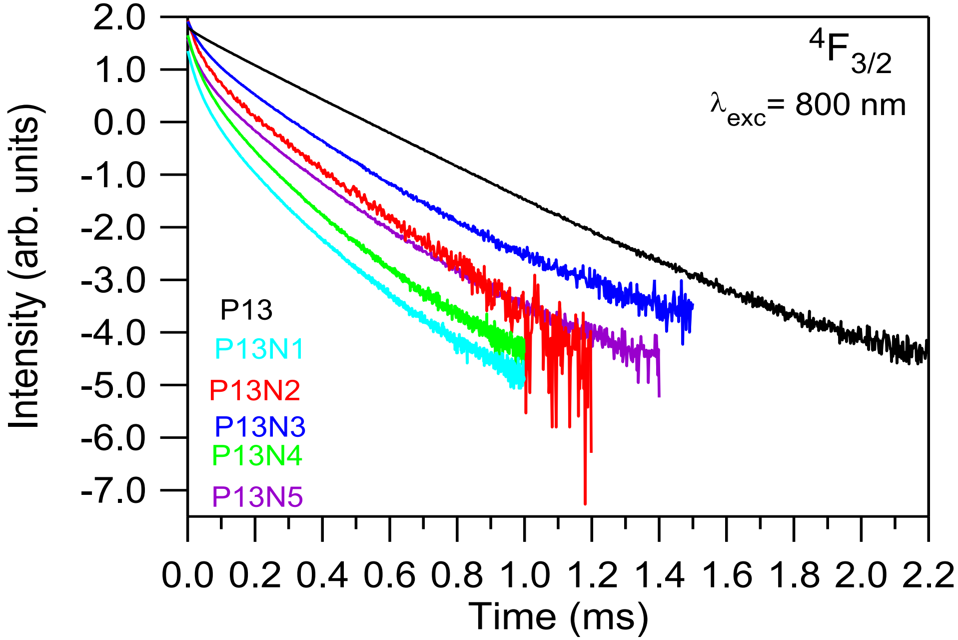


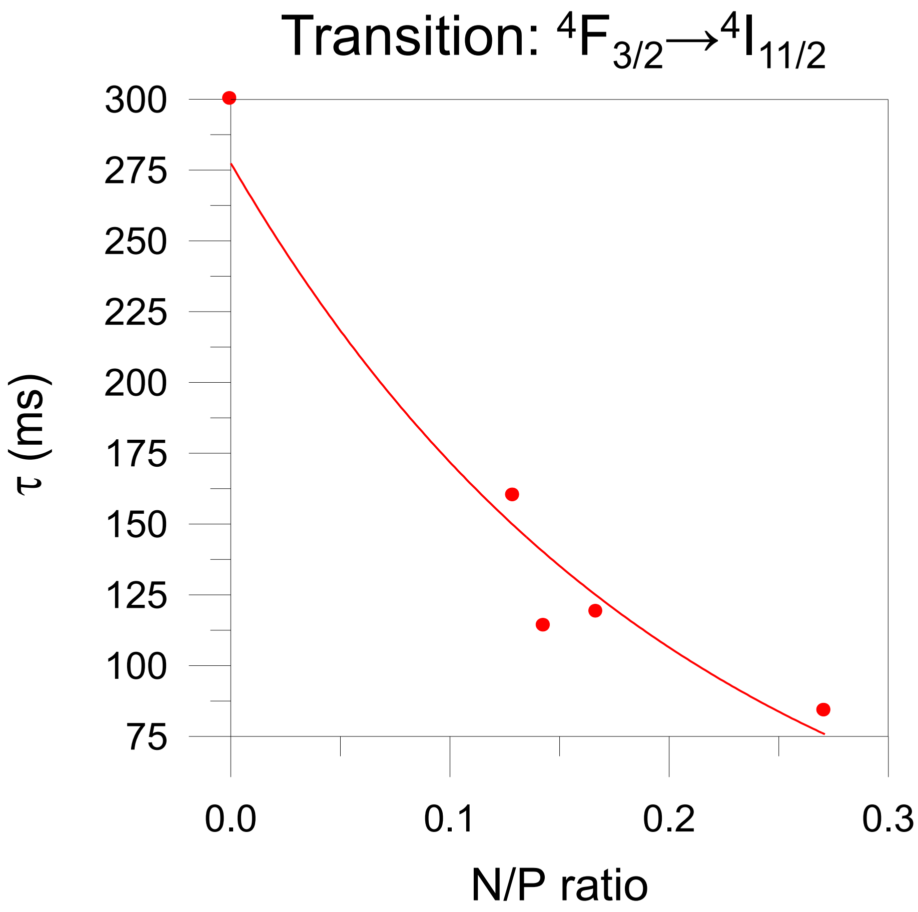




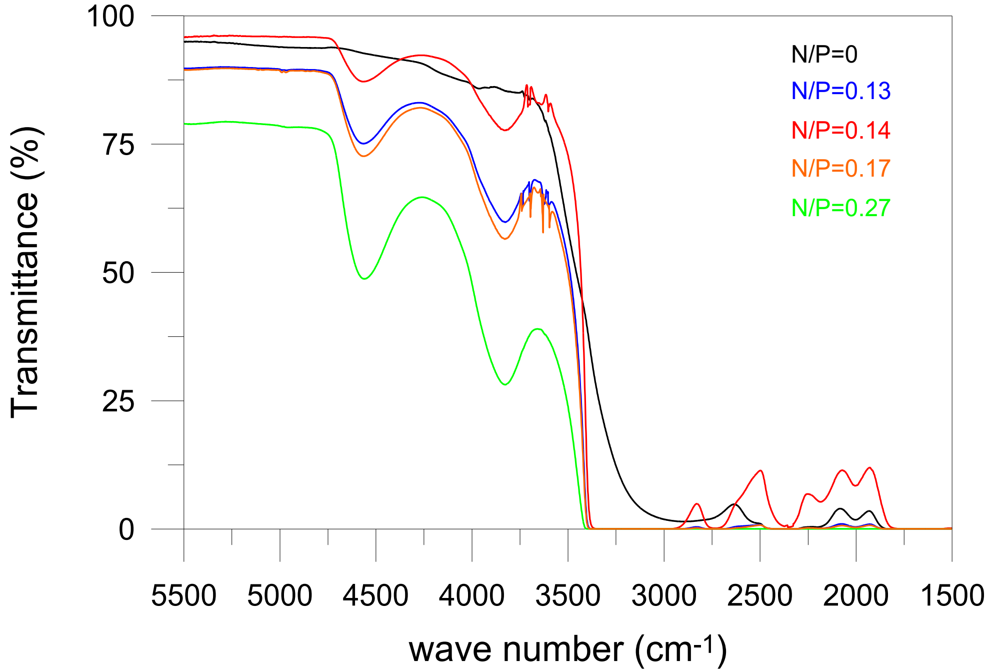
Nd-doped luminiscent oxynitride glasses



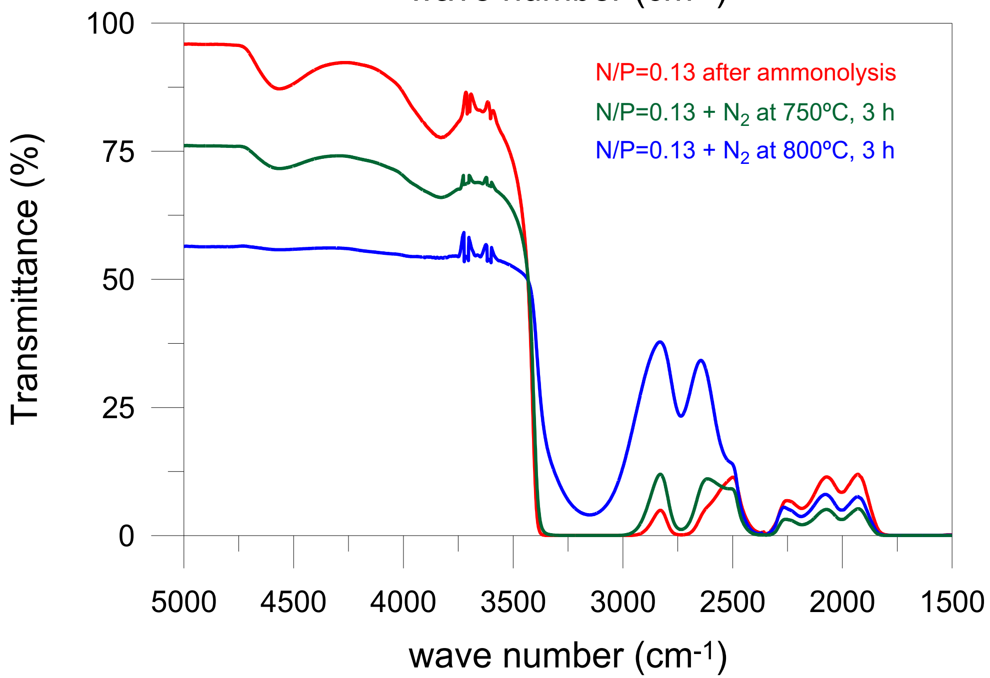




Nd-doped luminiscent oxynitride glasses



N-H and O-H bonds may contribute to
The non-radiative decay of the Nd3+
Fluorescence and make decrease the
Average lifetime



Thermal annealing at temperatures
Above the ammonolysis T can reduce
The water content in the glasses and
Improve their optical quality

Conclusions

- Nitrogen increases the glass-forming range
- Improves thermal and chemical stability
- Modifies diffusion depending properties
- Allows application of phosphates below T_g

Thank you for your attention

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CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

1988. Richard Brow & Mary Reidmeyer: NaPON, LiPON

N substitution without preference for BO and NBO oxygens

2000. André Le Sauze & Roger Marchand: LiNaPON

Random distribution of N, growing of oxynitride regions at the expense of the oxide regions

N_t = 3/2 BO, N_d = NBO + 1/2BO

2003. F. Muñoz, L. Pascual, A. Durán, L. Montagne & Roger Marchand

Mechanism of nitridation based on the preference for the oxygens near Pb^{2+} in LiNaPbPON

2006. F. Muñoz, L. Pascual, A., R. Berjoan & Roger Marchand: LiNaPbPON

XPS O_{1s} results on the N for O substitution following Marchand's rules

2013. F. Muñoz, L. Montagne, L. Delevoye, T. Charpentier

Distinction between BO and NBO in $P(O,N)_4$ tetrahedra

[J. Non-Cryst. Solids 363 (2013) 134]

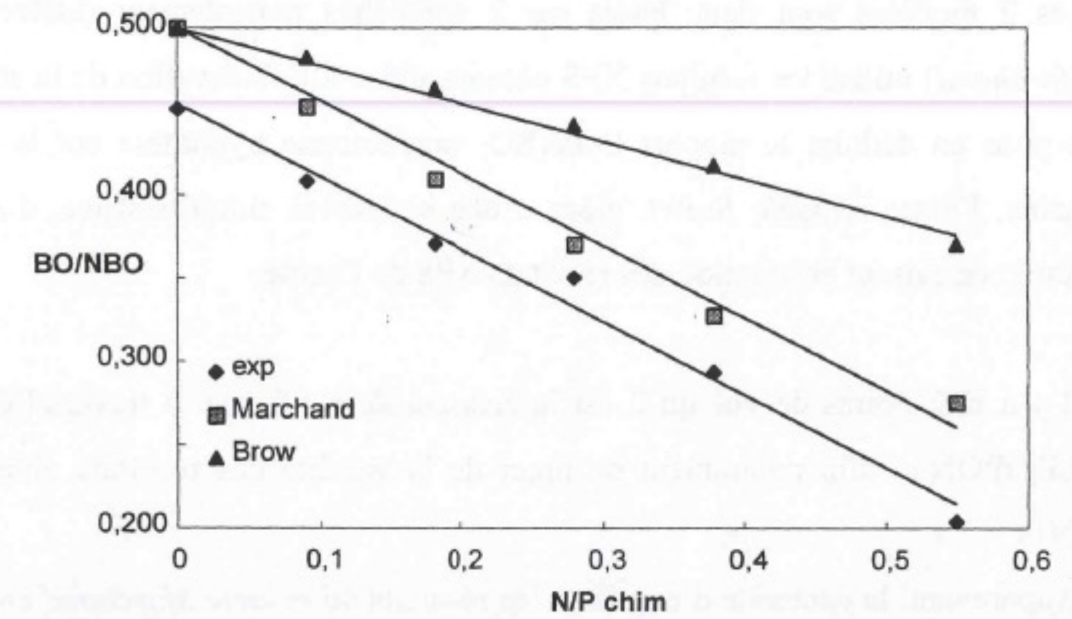
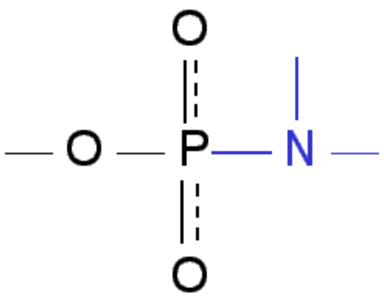
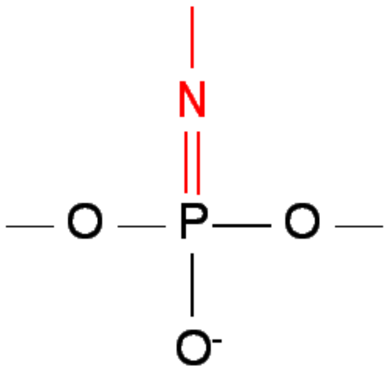


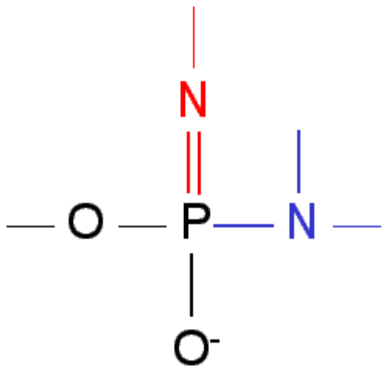
Figure II.23. : *comparaison de l'évolution des rapports BO/NBO expérimental et calculés à partir des modèles Marchand et Brow en fonction du rapport N/P obtenu par analyse chimique pour une série de verres « LiNaPON »*



PO_3N

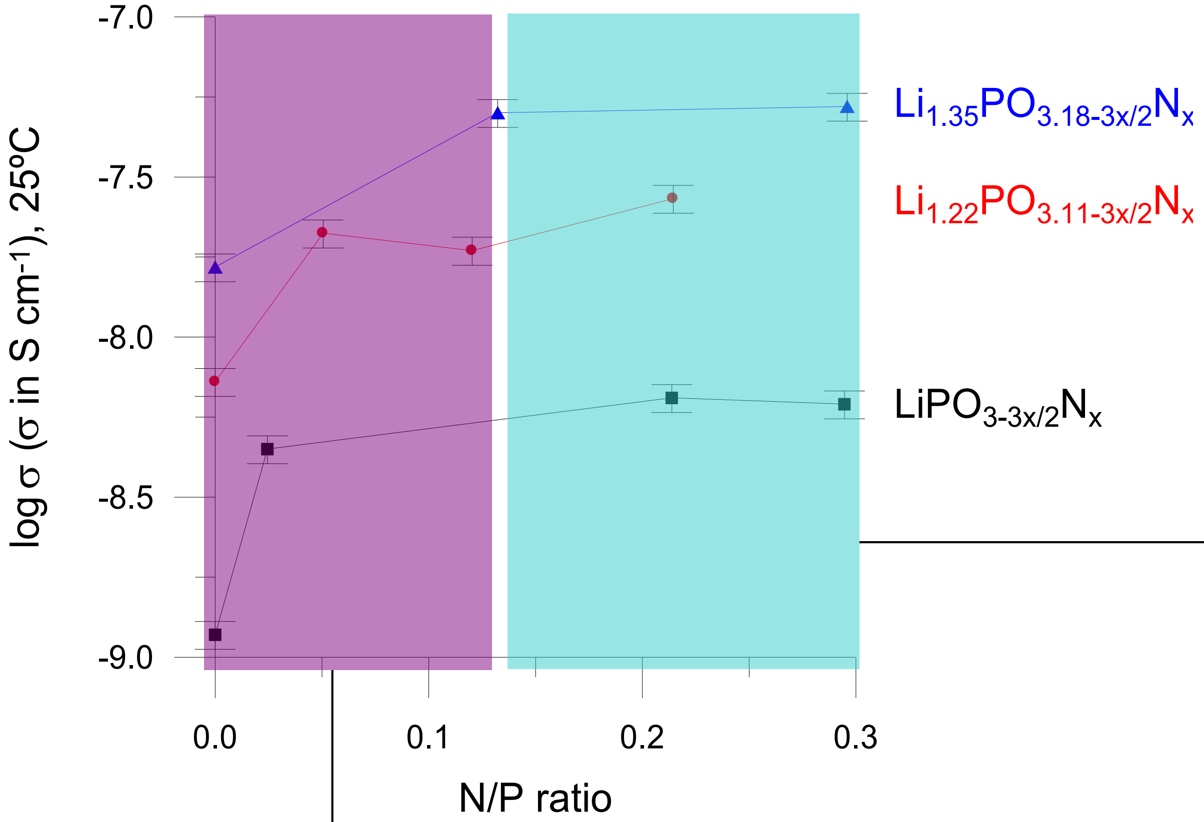


PO_3N



PO_2N_2

Oxynitride phosphate glasses: conductivity in LiPON glasses



↑ strength of Li-O

⇒ counteracts ↑ σ

Increase of non-bridging oxygens ⇒ ↑ σ

F. Muñoz et al., Solid State Ionics 179 (2008) 574

Structure of oxynitride glasses

Zeyer *et al.* JNCS 311 (2002) 223

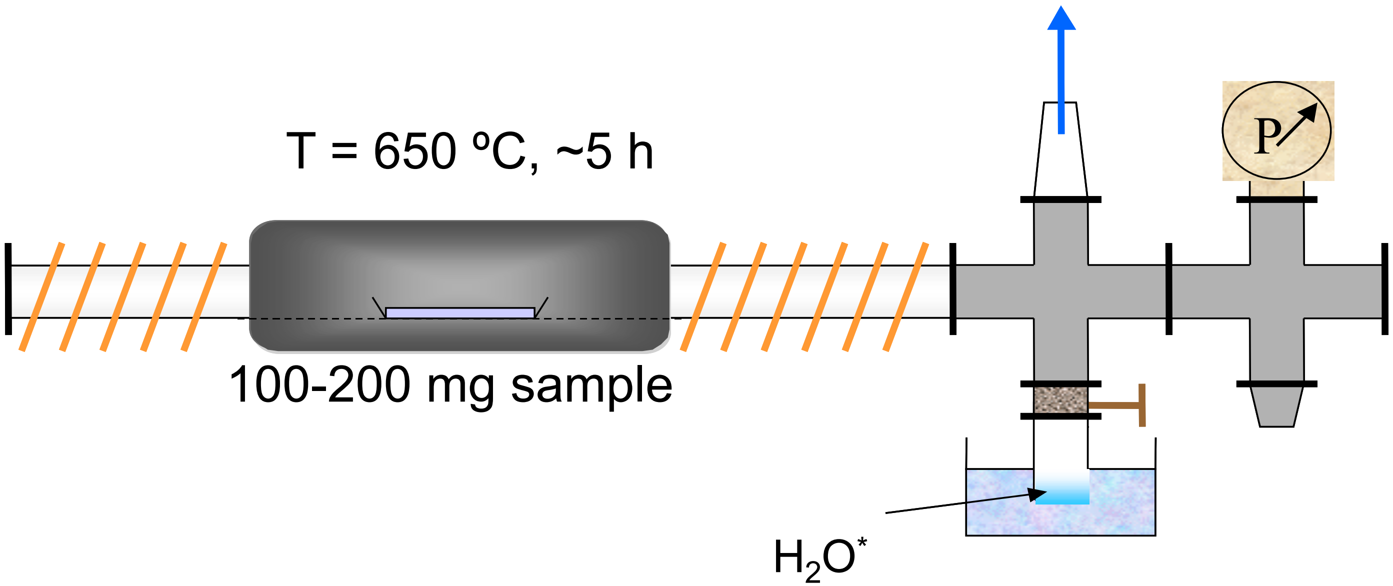
<< T + Ar ⇒ 80ºC

$$PCl_5 + 4H_2O^* \rightarrow H_3PO^*_4 + 5HCl$$

500ºC

$$H_3PO^*_4 + Na_2CO_3 \rightarrow NaH_2PO^*_4 + CO_2 + H_2O \rightarrow NaPO^*_3$$

Flambard *et al.* Chem. Comm. (2006) 3426



- Easier and chepear than hydrolysis from $H_3PO^*_4$
- Simultaneous enrichment of several different samples
- Valid for either crystalline or glassy materials

Phosphate glasses in biodegradable composite materials

- Congruent dissolution in aqueous media
- Control of the dissolution rate
- Glass formulation with bio-compatible elements

Applications

Reinforcement with polymers and calcium phosphate cements

Phosphate glass fibers

Drugs release; Antibacterial effect, antimicrobial (Ga, Cu, Ag)

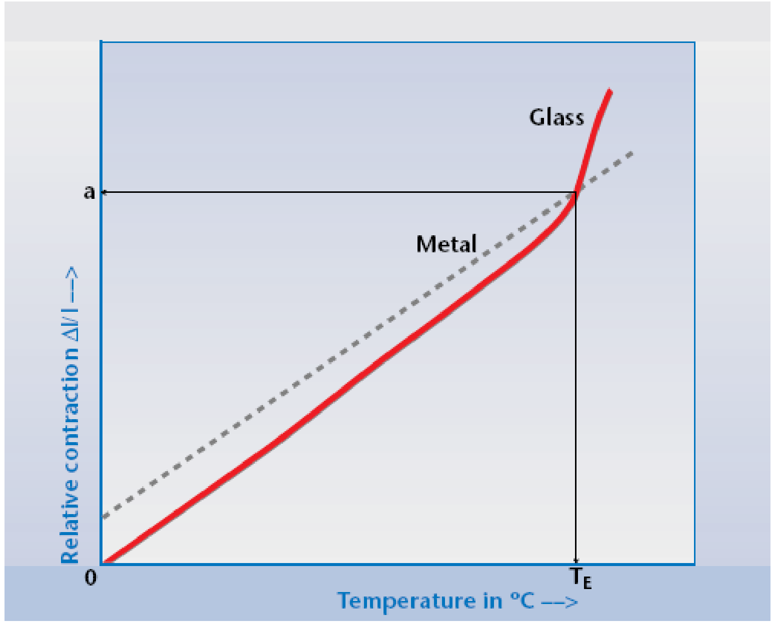
Fluorine release for reparation in odontology

Increase of chemical durability → + Fe, Al

Knowles J.C. *et al.*, J. Mater. Chem. 13 (2003) 2395
Valappil S.P. *et al.*, Adv. Func. Mater. 18 (2008) 732
Abou Neel E.A. *et al.*, J. Mater. Chem. 19 (2009) 690
Lin S.T. *et al.*, Biomaterials 15(13) (1994) 1057

Low temperature sealing glasses

TV solder glasses: $BaO\text{-}PbO\text{-}ZnO\text{-}B_2O_3\text{-}SiO_2$
PbO must be substituted : Low softening T and high CTE



source: *SCHOTT technical handbook*

1. Sealing temperature $T < T_m$ melting temperature
2. Viscosity: $\log \eta = 3 – 5$
3. Adjust coefficient of thermal expansion

   $\Delta\alpha = \alpha_m - \alpha_g = 0.5 – 1.10^{-6}\ K^{-1}$
5. Minimize residual tensions
5. High chemical durability at the same time
6. Low thermal expansion
7. High electrical resistance