An interpretation for the increase of ionic conductivity by nitrogen incorporation in LiPON oxynitride glasses

Nerea Mascaraque\textsuperscript{a}, José Luis G. Fierro\textsuperscript{b}, Alicia Durán\textsuperscript{a}, Francisco Muñoz\textsuperscript{a,*}

\textsuperscript{a}Instituto de Cerámica y Vidrio (CSIC), Kelsen 5, 28049 Madrid, Spain

\textsuperscript{b}Instituto de Catálisis y Petroquímica (CSIC), Marie Curie 2, 28049 Madrid, Spain

*fmunoz@icv.csic.es

Abstract

The influence of nitrogen in the mechanism of ionic conduction has been studied in lithium phosphorus oxynitride glasses with composition xLi\textsubscript{2}O.(100-x)P\textsubscript{2}O\textsubscript{5} (x = 38-60 mol.%). A correlation between glass structure and ionic conductivity has been established for explaining the conduction mechanism. The change of glass structure during nitridation has been studied as a function of lithium and nitrogen contents. Raman spectra confirm the increase of P\textsubscript{2}O\textsubscript{7}\textsuperscript{4-} groups with increasing lithium and the presence of nitrogen, as also shown by X-Ray Photoelectron Spectroscopy. The O\textsubscript{1s} core-level XPS spectra allow determining the variation of the bridging (BO) to non-bridging (NBO) oxygens ratio, observing that its decrease is directly linked to an increase of ionic conductivity. The ionic conductivity of oxynitride glasses is higher than that of their parent phosphate glasses, although this increase also depends on the lithium content. Furthermore, it has been demonstrated that the influence of nitrogen is higher in glasses with smaller amount of lithium. These findings will contribute to the design of glasses with lower lithium contents and high ionic conductivity for their application as solid electrolytes in lithium rechargeable batteries.

**Keywords:** phosphate glasses; oxynitride glasses; Raman; XPS; ionic conductivity; LiPON; solid electrolytes.
**Introduction**

Phosphate glasses have gained a great interest during the last decades due to their properties, becoming good candidates for different potential applications. Generally, the main characteristics of phosphate glasses are their low dilatometric softening and glass transition temperatures, high thermal expansion coefficient, as well as high refractive index and transparence in UV. Depending on their properties, phosphate glasses can be applied as matrices for vitrification of radioactive wastes [1], sealing elements in low temperature sealings [2], matrices for generation of laser radiation [3] and solid electrolytes for lithium rechargeable batteries [4-6]. The improvement of their properties, such as the ionic conductivity, chemical durability or thermal stability, is an important aim for the application of lithium phosphate glasses as solid electrolytes in lithium batteries, which could be achieved through the introduction of nitrogen [7-12].

Bates and co-workers developed a new amorphous thin film of lithium phosphorous oxynitride, the so-called LiPON [4], with a suitable ionic conductivity ($\sim 2 \times 10^{-6}$ S·cm$^{-1}$), which is prepared by RF Magnetron Sputtering from crystalline Li$_3$PO$_4$. Nevertheless, no concluding interpretation has been given to the effect of nitrogen on the ionic conductivity of the LiPON thin films, even though the modification of the conductivity of the thin films has been related to that occurring in bulk Li$_2$O-P$_2$O$_5$ glasses with nitrogen. Several attempts to explain the improvement of ionic conductivity by nitrogen/oxygen substitution have pointed to the decrease of electrostatic energy of LiPON with respect to the Li$_3$PO$_4$ reference material [8], or the increasing amount of three-coordinated nitrogen species, N$_t$ (-N<) in the films [13]. The starting material, crystalline Li$_3$PO$_4$, has a composition which is not possible to obtain in glassy bulk form due to the high Li$_2$O content that leads to the devitrification upon cooling the melt [14]. Lithium phosphorus oxynitride glasses can be easily prepared by ammonolysis [11, 12], a procedure based on the thermal treatment below 800°C of the parent phosphate glass.
under ammonia flow, which is feasible up to a composition of 58 mol.% of Li$_2$O. During nitridation, new structural units are formed as a consequence of the anionic network modification, PO$_3$N and PO$_2$N$_2$ [8, 15, 16]. It has been proposed that oxygen substitution by nitrogen produces an increase in conductivity, likely due to an increase in the non-bridging oxygens content, along with an increase in the connectivity of the glass network [12] by the formation of P-N and P=N bonds, which have higher covalent character as compared to P-O bonds. Recently, as studied by Muñoz et al. in glasses with composition $x$Li$_2$O.$(1-x)$P$_2$O$_5$ ($x\geq0.5$) [12], it has been shown that the conductivity does not present a linear behaviour as a function of nitrogen content. The conductivity increases with nitridation up to a maximum value, which has been proposed to occur as a consequence of the decrease of the bridging to non-bridging oxygen ratio that occurs with substitution of nitrogen for oxygen. With further nitridation, the conductivity remains nearly constant as a consequence of a change in the lithium environment, as observed by $^6$Li NMR spectroscopy [12], which leads to a higher covalent character of Li-O bonds and could counteract the increase in the conductivity.

The present work is focused on the preparation of lithium phosphorus oxynitride glasses within a wider composition range in order to demonstrate how nitrogen affects the ionic conductivity and its relationship with the glass structure.

1. Experimental

1.1 Preparation of the glasses

The lithium phosphate glasses belong to the system Li$_2$O-P$_2$O$_5$ and were prepared by melt-quenching technique from batches of reagent grade materials: Li$_2$CO$_3$ (99 % ACS. Reagent, Aldrich) and (NH$_4$)$_2$HPO$_4$ (99 % ACS. Reagent, Merck). The batches were calcined in porcelain crucibles in an electric furnace up to 400 °C during 1 day, then melted during 2 h at temperatures ranging from 800 °C to 850 °C, depending on their composition. The glasses
were obtained by pouring the melts onto brass plates. They were annealed slightly above their glass transition temperature \( T_g \), which was previously determined by Differential Thermal Analysis (DTA). Finally, the glasses were nitrided following a thermal treatment under anhydrous ammonia at 750 °C during different length of time (2, 4 and 7 h). The glass with composition \( 60\text{Li}_2\text{O}.40\text{P}_2\text{O}_5 \) devitrified during nitridation, so it was necessary to use an alternative route that consisted on a two-steps melting process. A glass with composition \( 55\text{Li}_2\text{O}.45\text{P}_2\text{O}_5 \) and their oxynitride glasses were first prepared, as shown previously. Then, the oxynitride glasses were re-melted at 900°C with an increased amount of lithium carbonate under a nitrogen flow to avoid nitrogen losses.

### 1.2 Characterisation of the glasses

Nitrogen analyses were carried out in a nitrogen/oxygen LECO TC-436 analyser by the inert gas fusion method. N/P is calculated through the following equation

\[
\frac{N}{P} = \frac{M_{\text{base glass}} \cdot \text{wt.\%N}}{10 \cdot (140 + \text{wt.\%N})}
\]

being \( M_{\text{base glass}} \) molecular weight of the glass without nitrogen and \( \text{wt.\%N} \) is the weight percentage of nitrogen obtained by the LECO TC-436 analyser. The maximum deviation in the N/P atomic ratio is ± 0.02 N/P units.

The density \( (\rho) \) of the glasses was measured at room temperature using the Archimedes method. The weight of each glass was measured in air and in distilled water using a balance measuring to ±0.1 mg. The molar volume \( (V_m) \) was calculated from the obtained density data using the following equation (2):

\[
V_m = \frac{M}{\rho}
\]

being \( M \) the molecular weight of the glass and \( \rho \) the density.

The glass transition temperature has been determined by Differential Thermal Analysis (DTA) in a SEIKO – 6300 ATD/TG analyser, using a platinum crucible, a constant heating
rate of 10 °C/min under air flow and in the temperature range from 25 to 800°C. The glass transition temperature is determined at the onset of the endothermic effect shown in the DTA patterns, and the error in $T_g$ is taken to be within ± 5°C.

Ionic conductivity measurements were performed in a VMP3 impedance analyser from BioLogic, in the frequency range from 10 Hz to 1 MHz at temperatures between 25 and 180°C. The electrodes were obtained by painting both faces with silver paste (Silver conductive paint, Electrotube®). The Nyquist plot of complex versus real impedance allows determining the samples resistance (R) which is read to the intersection point with the horizontal axis. The conductivity is calculated using the equation:

$$\sigma = \frac{(l/R) \cdot (l/A)}{\text{horizontal axis}}$$

being $l/A$ the sample geometric factor, where $l$ is thickness and $A$ is sample area.

Raman measurements were performed using a confocal Raman microscope coupled to an AFM (Witec alpha-300R) on polished surface of bulk glasses at room temperature. Raman spectra were obtained using a 532 nm excitation laser and a 100x objective lens (NA = 0.9). The incident laser power was 0.5 mW and the Raman spectral resolution of the system is 0.02 cm$^{-1}$.

Photoelectron spectra (XPS) were obtained with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyser and a MgKα ($\text{hν} = 1254.6$ eV, $1 \text{ eV} = 1.6302 \times 10^{-19}$ J) X-ray source, powered at 120 W. The kinetic energies of photoelectrons were measured using a hemispherical electron analyser working in the constant pass energy mode (pass energy of 20 eV). The background pressure in the analysis chamber was kept below $8 \times 10^{-9}$ mbar during data acquisition. The XPS data signals were taken in increments of 0.1 eV with dwell times of 50 ms. Binding energies were calibrated relative to the C 1s peak at 284.9 eV. High resolution spectra envelopes were obtained by curve fitting synthetic peak components using the software “XPS peak”. The raw data were used with no preliminary smoothing. Symmetric
Gaussian-Lorentzian functions were used to approximate the line shapes of the fitting components. Atomic ratios were computed from experimental intensity ratios and normalized by atomic sensitivity factors [17].

2. Results

2.1. Glass Properties

Table I shows the nitrogen content in wt. % and the formula for all studied glasses. For a constant nitridation temperature of 750ºC, the nitrogen content of the glasses depends on the nitridation time. This content increases with increasing time, i.e. glasses with Li₂O higher than 50 mol % show higher nitrogen contents. This could be interpreted in terms of the decrease of the melt viscosity for higher lithium containing glasses that could allow the introduction of higher nitrogen contents, as previously shown in alkali-lead oxynitride phosphate glasses [18].

In Figure 1, the molar volume of glasses with composition xLi₂O.(100-x)P₂O₅ + nitrogen (x = 38, 45, 55) is shown as a function of the N/P ratio. A decrease of molar volume is observed for increasing lithium content in the base glasses, while the introduction of nitrogen produces a slight decrease of Vₘ in the three series.

Figure 2.a) gathers the glass transition temperature for xLi₂O.(100-x)P₂O₅ (x = 38, 45, 50, 55) glasses as a function of lithium oxide. For compositions between 38 and 50 mol. % Li₂O, Tₙ increases with increasing lithium content due to the increase of cross-linking by O-Li-O covalent bridges, as shown by others authors [19, 20]. However, for glasses with lithium contents higher than 50 mol. %, the Tₙ is almost constant, likely due to a higher depolymerisation by the transformation of Q² into Q¹ structural units [12].

Figure 2.b) represents the glass transition temperature for xLi₂O.(100-x)P₂O₅ + nitrogen (x = 38, 45, 50, 55) glasses as a function of N/P ratio. The introduction of nitrogen produces the increase of Tₙ as a consequence of the increasing bonding density due to the formation of new
P-N bonds. Lower lithium containing glasses show the highest increase of $T_g$ with nitrogen. In the four series, the increase of $T_g$ is almost linear.

Figure 3 presents the logarithm of ionic conductivity at room temperature as a function of lithium content in the studied lithium phosphate glasses without nitrogen. The log of $\sigma_{25^\circ C}$ increases with increasing lithium oxide content, being this increase linear for glasses with composition from 45 to 60 mol. % of Li$_2$O. The results are similar to those observed by Martin et al. [21]. Figure 4 depicts the logarithm of ionic conductivity at room temperature as a function of N/P ratio for all studied lithium oxynitride phosphate glasses. The introduction of nitrogen in all glasses produces an increase of ionic conductivity that also depends on the amount of lithium. It is observed that for glasses with lower lithium contents the increase in conductivity is much more significant, though, obviously, the glasses with 60 mol % Li$_2$O present the highest ionic conductivities due to the higher amount of Li$^+$ mobile ions. An N/P ratio of 0.25 has been fixed to determine the influence of nitrogen as a function of lithium content in oxynitride glasses. Figure 5 represents the difference between log $\sigma_{25^\circ C}$ of oxynitride glasses with N/P=0.25 and their corresponding base glasses. It can be seen that for glasses with higher lithium content, the increase of conductivity induced by nitrogen is only 0.55 orders of magnitude, meanwhile for glasses with 38 mol. % Li$_2$O the conductivity increase is around 2 orders of magnitude. The increase in the oxynitride glass with 60 mol % Li$_2$O is higher than that of the 55 mol % one, which could be due to the fact that these glasses were prepared following a different melting process where some excess lithium might have remained. Figure 6 gathers the activation energy for conduction in lithium phosphorus oxynitride glasses with composition $x$Li$_2$O.$(100-x)$P$_2$O$_5$ + Nitrogen ($x = 38$ - 60 mol. %). The increase of nitrogen content produces the decrease of activation energy, being this decrease more significant in glasses with lower lithium and nitrogen contents.
Figure 7 displays the Raman spectra of oxynitride glasses with 55 mol. % of Li$_2$O. The spectra show several bands corresponding to phosphorus-oxygen [19, 22] and phosphorus-nitrogen [7, 23] groups which are active in Raman. Table II shows the peaks assignment for Li$_2$O-P$_2$O$_5$ and LiPON Raman Spectra by other authors. The assignments of P-N groups are supported by comparisons with spectra from model phosphazene compounds, and isotope shifts observed in nitrided glass samples made with $^{15}$N labeled ammonia [24]. The bands corresponding to P-O-P, P$_2$O$_7^{4-}$, PO$_2$ and P=O, appear at 735, 1020, 1170 and 1250 cm$^{-1}$, respectively. In the oxynitride glasses, new bands appear at 630 and 830 cm$^{-1}$ which correspond to three-coordinated (P-N<(P)$_2$) and two-coordinated nitrogen (P-N=P), respectively. In lithium and sodium metaphosphate glasses [7], the introduction of nitrogen produces the shift of P=O band toward lower Raman shift (cm$^{-1}$) due to the substitution of the less electronegative nitrogen for oxygen. However, the position of PO$_2$ bands is maintained constant, which suggests that the incorporated nitrogen does not affect this bond for these compositions [7]. The oxynitride glasses with 38 and 45 mol. % Li$_2$O studied in this work present the same behaviour (not shown). However, for higher lithium containing glasses, e.g. 55 mol. % Li$_2$O, a slight shift of PO$_2$ bands toward lower Raman shift (cm$^{-1}$) is also observed with increasing nitrogen content. The shift of P=O and P-O-P between base glasses and their corresponding oxynitrides with the highest nitrogen content is around 5 cm$^{-1}$. Besides, it is observed that the increase of nitrogen content produces the decrease of % P-O-P and an increase of P$_2$O$_7^{4-}$, as previously shown by Le Sauze in LiNaPON and NaPON glasses [25].

XPS measurements have been performed for glasses with composition xLi$_2$O.(100-x)P$_2$O$_5$ + nitrogen (x=45, 50, 55), only one series being shown as example. Figure 8 shows the XPS spectra in the binding energy region of the N$_{1s}$ peak of glasses with composition 45Li$_2$O.55P$_2$O$_5$ + nitrogen. These spectra are deconvoluted into two Gaussian-Lorentzian
mixed components attributed to two different bonding states of nitrogen atoms [8, 26-28]. The first one (N_d) is bound to two phosphorus atoms (P-N=P) and appears at 397.7 eV, whilst the second one (N_t) corresponds to a nitrogen atom linked to three phosphorus atoms (P-N<(P)_2) and appears at 399.9 eV. The increase in nitrogen content produces the decrease of N_t, almost disappearing for the highest nitrogen content (N/P=0.27) in these glasses. Figure 9 represents the N_t/N_d ratio as a function of N/P ratio obtained from the deconvolution of XPS spectra for the samples. A decrease of N_t/N_d ratio is observed with increasing nitrogen content, the decrease of this ratio being more significant in glasses with higher lithium content. Besides, three-coordinated nitrogen is predominant in glasses with high lithium and low nitrogen content.

Figure 10 depicts the XPS spectra in the binding energy region of the O_1s peak of glasses with composition 45Li_2O.55P_2O_5 + nitrogen. These spectra are deconvoluted in three Gaussian-Lorentzian mixed components attributed to two non-bridging oxygens (NBO), P=O and Li+…-O-P, at 531.4 and 532.3 eV, respectively, and bridging oxygens (BO) at 533.5 eV, according to the models of Marchand [26] and Brückner [29]. It is observed that the nitrogen introduction produces the decrease of BO and increase of NBO.

Figure 11 shows the BO/NBO ratio versus N/P ratio obtained from the deconvolution of the three bands, observing a decrease of BO/NBO ratio with increasing nitrogen content; this decrease being higher for glasses with lower lithium content. However, in 55 mol. % of Li_2O glasses, the BO/NBO ratio is nearly constant. Besides, the inset of Fig. 11 shows the decrease of BO/NBO with increasing lithium oxide content in base glasses, according to the increase in ionic conductivity for glasses with composition comprised between 45 and 55 mol % Li_2O (Fig. 5).

3. Discussion
In the glasses studied in this work, the introduction of lithium and nitrogen in the phosphate glass network leads to a decrease of molar volume and the increase of the glass transition temperature (Fig.1-3). The model of Anderson and Stuart [30] establishes that the activation energy of conduction depends on two terms, i.e. the network strain energy and the electrostatic energy change. According to the model of Anderson and Stuart, it can be thought that the increased bonding density and network reticulation caused by the formation of the P-N bonds would be at the source of an increase of the term related to network strain energy, i.e. the increase of activation energy. However, a decrease of $E_a$ is observed with increasing lithium content, and for lower amounts of nitrogen, in particular (Fig.6). As proposed by Wang [8], the replacement of P–O bonds by the more covalent P–N ones may cause the decrease in the electrostatic activation energy that could counteract the increase of network strain energy, leading to an effective decrease of $E_a$.

The presence of the new P-N bonds was verified by Raman spectroscopy and by the binding energies of $N_{1s}$ peak, as shown Fig. 7 and 8. The introduction of nitrogen in glasses with different lithium content produces the decrease of the percentage of P-O-P bonds, with an increase of $P_2O_7^{4-}$. These results confirm those of Le Sauze in LiNaPON and NaPON glasses, relating the increase of $P_2O_7^{4-}$ to an increase of nitrogen content [25].

The $O_{1s}$ and $N_{1s}$ core-level spectra permit a detailed study of the glass structure, allowing a deeper knowledge of the mechanism of ionic conduction. In all the series, an increase of nitrogen content produces an increase of ionic conductivity; however, in glasses with lower lithium content, this increase is around two orders of magnitude, being of only 0.45 orders of magnitude for the glass with 55 mol. % of $Li_2O$. From the $O_{1s}$ core-level spectra, the relationship between BO and NBO is shown to decrease with increasing nitrogen content, as expected [31, 32]. But the decreasing rate depends on the lithium content (Fig.11). This decreasing rate may be related to the magnitude of the decrease of BO/NBO ratio between a
glass with a given nitrogen content and the oxide glass. The inset in Fig. 11 shows the difference between the BO/NBO ratio for the glasses with N/P=0.25 and that of the glasses with N/P=0 against the mol % Li₂O. Thus, it can be seen that the higher the lithium content the lower the decrease of the BO/NBO ratio with nitrogen. A good correlation can be established between the decrease of the BO/NBO ratio and the ionic conductivity in the three oxynitride series of glasses. Indeed, the conductivity increases with the decreasing BO/NBO ratio as it was previously proposed in [12].

From the N₁s core-level spectra, the variation of the Nₙ/Nₖ ratio as a function of introduced nitrogen was studied. An increase of Nₙ with increasing nitrogen content has not been observed in the glasses studied in this work in relationship with an increase in the ionic conductivity as in the thin films [13]. In the phosphate base glasses, the Nₙ is predominant and decreases with increasing nitrogen content. But, glasses showing a slighter decrease of Nₙ/Nₖ ratio present higher increase of NBO, as well as bigger increase of ionic conductivity with increasing N/P ratio. The formation of a higher amount of Nₙ, or Nₖ, depends basically on the initial distribution of oxygens in BO and NBO. This variation of Nₙ/Nₖ is explained from Marchand rules [26] that establish the following equations:

\[ Nₙ = \frac{3}{2}BO \]  \hspace{1cm} (4)
\[ Nₖ = 1NBO + \frac{1}{2}BO \]  \hspace{1cm} (5)

The three-coordinated nitrogen is formed from bridging oxygens (Equation (4)), so for glasses with lower lithium content a decrease of BO/NBO and Nₙ/Nₖ ratios is observed, also confirming the direct relationship between ionic conductivity and glass structure.

In this work, a direct relationship between the ionic conductivity and the structural changes in oxynitride phosphate glasses has been proposed. It has been demonstrated that the increase of conductivity by nitrogen incorporation is higher for glasses with lower lithium contents,
which can be explained throughout the decrease of the BO/NBO ratio taking place during the course of the nitridation.

4. Conclusions

The introduction of nitrogen in lithium phosphate glasses produces the increase of the glass transition temperature due to increase of bonding density and the formation of P-N bonds, together with a decrease of molar volume. It has been shown that the increase of ionic conductivity with nitrogen content also depends on lithium content, observing that in glasses with lower lithium contents a higher increase of conductivity is produced for the same nitrogen content. This behaviour is explained through the variation of the BO/NBO ratio. The lower the lithium content the higher the decrease of BO/NBO ratio, which results in a higher difference in the room temperature conductivity between the oxide and oxynitride glass.

Acknowledgements

Financial support from project MAT2010-20459 of Ministerio de Ciencia e Innovación is greatly acknowledged. N. Mascaraque thanks Ministerio de Economía y Competitividad for funding of a FPU-2009. The authors are also very grateful to Dr. Adolfo del Campo from ICV-CSIC for his support in the Raman characterization.
References


**Figure captions**

Figure 1: Molar volume determined by equation (2) as a function of N/P ratio for the glasses with composition xLi$_2$O.(100-x)P$_2$O$_5$ + nitrogen, where x = 38, 45, 55. Lines are drawn as guides for the eyes.

Figure 2: Glass transition temperature as a function of lithium oxide (a)) and nitrogen-phosphorus ratio (b)) in the glasses with composition xLi$_2$O.(100-x)P$_2$O$_5$, where x = 38, 45, 50, 55. Lines are drawn as guides for the eyes.

Figure 3: Log ionic conductivity at 25 ºC as a function of lithium oxide content (in mol %) for the glasses with composition xLi$_2$O.(100-x)P$_2$O$_5$, where x = 38-60. Error bars are of the size of the symbols. Lines are drawn as guides for the eyes.

Figure 4: Log $\sigma$ at 25ºC as a function of nitrogen-phosphorus ratio for the glasses with composition xLi$_2$O.(100-x)P$_2$O$_5$ + nitrogen, where x = 38-60. Error bars are of the size of the symbols. Lines are drawn as guides for the eyes.

Figure 5: Variation of the increase of Log $\sigma$ at 25 ºC in oxynitride glasses with a fixed N/P ratio of 0.25 with respect to the conductivity value in the oxide glasses, xLi$_2$O.(100-x)P$_2$O$_5$, as a function of x = Li$_2$O, where x = 38-60. Line is drawn as a guide for the eyes.

Figure 6: Activation energy as a function of nitrogen-phosphorus ratio in the glasses with composition xLi$_2$O.(100-x)P$_2$O$_5$, where x = 38-60. Lines are drawn as guides for the eyes.

Figure 7: Raman spectra of 55Li$_2$O.45P$_2$O$_5$ glass and their three oxynitride glasses, together with a magnification in the region comprised between 600 and 900 cm$^{-1}$.

Figure 8: N$_{1s}$ core-level spectra of xLi$_2$O.(100-x)P$_2$O$_5$ + nitrogen, where x = 45, 50, 55, glasses.

Figure 9: The relationship between three-coordinated nitrogen (N$_t$) and two-coordinated nitrogen (N$_d$) as a function of N/P ratio, for glasses with composition xLi$_2$O.(100-x)P$_2$O$_5$ + nitrogen, where x = 45, 50, 55. Lines are drawn as guides for the eyes.
Figure 10: O$_{1s}$ core-level spectra of xLi$_2$O.(100-x)P$_2$O$_5$ + nitrogen, where x = 45, 50, 55, glasses.

Figure 11: The relationship between bridging oxygen (BO) and non-bridging oxygen (NBO) as a function of N/P ratio, for glasses with composition xLi$_2$O.(100-x)P$_2$O$_5$ + nitrogen, where x = 45, 50, 55. The inset represents the difference of BO/NBO ratio between the oxynitride glasses for N/P=0.25 and that of the oxide glass against of mol % Li$_2$O. Lines are drawn as guides for the eyes.

Table captions

Table I: Weight % of nitrogen and formula of the all studied glasses.

Table II: Raman shifts in Li$_2$O-P$_2$O$_5$ and LiPON glasses.
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
55Li₂O·45P₂O₅

Raman Shift (cm⁻¹)

N/P=0.27
N/P=0.21
N/P=0.11
N/P=0

Figure 7
Figure 8

$45\text{Li}_2\text{O} \cdot 55\text{P}_2\text{O}_5$

- - - - - Experimental

- - - - - Fit

N/P = 0.27

N/P = 0.21

N/P = 0.11

Binding energy (eV)
Figure 9
Figure 10
Figure 11
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<td>Li(<em>{0.82})PO(</em>{2.51})N(_{0.27})</td>
<td>60/40N7</td>
<td>5.4</td>
<td>Li(<em>{1.5})PO(</em>{2.83})N(_{0.28})</td>
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</tbody>
</table>
Table II

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Raman Shift (cm$^{-1}$)</th>
<th>Reference</th>
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</thead>
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<tr>
<td>P-N&lt;(P)$_2$</td>
<td>601-625</td>
<td>[33]</td>
</tr>
<tr>
<td>P-O-P</td>
<td>677-777</td>
<td>[22]</td>
</tr>
<tr>
<td>P-N=P</td>
<td>802</td>
<td>[33]</td>
</tr>
<tr>
<td>P$_2$O$_4^{+}$</td>
<td>1019</td>
<td>[4]</td>
</tr>
<tr>
<td>O-P-O</td>
<td>1148</td>
<td>[4]</td>
</tr>
<tr>
<td>P=O</td>
<td>1280-1390</td>
<td>[22]</td>
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</tbody>
</table>