Composition and structure dependence of the properties of lithium borophosphate glasses showing boron anomaly

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Abstract

This work presents a study on the structure, microstructure and properties of 50Li2O.xB2O3.(50-x)P2O5 glasses. The structure has been studied through NMR spectroscopy and the microstructure by TEM. The properties of the glasses are discussed according to their structure and microstructural features. The introduction of boron produces new linkages between phosphate chains through P-O-B bonds, whose amount increases with boron incorporation; at the same time, a depolymerisation of the phosphate chains into Q1-type phosphate units takes place. The introduction of boron produces an increase in Tg together with a decrease in the molar volume. The room temperature electrical conductivity increases with boron content as well. However, B2O3 contents higher than 20 mol % lead to crystallisation of lithium orthophosphate which contributed to hinder ionic conduction of the glasses.

Keywords: Phosphate glasses; Boron; MAS-NMR; Electrical conductivity

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1. Introduction

The development of solid electrolytes for lithium secondary batteries has become an interesting topic for many researchers of the glass community in the exploration of novel technological applications of glassy materials [1-5]. The use of solid materials as electrolyte components of the battery could avoid several drawbacks like those related to contamination of the electrode materials and explosions when using liquid electrolytes [6,7]. The general requirements that solid electrolytes must fulfil are: a high ionic conductivity of lithium ions at room temperature, negligible electronic contribution together with chemical and mechanical stability within the working potential range, and compatibility with the electrode materials.

Nowadays, the most promising glassy electrolytes which have already been tested in rechargeable battery devices belong to systems of composition LiI-LiF-Li₂S-Li₂O-P₂O₅-P₂S₅ with many possible variations [8,9]. Glasses of these systems possess conductivities as high as $10^{-3}$ S.cm$^{-1}$ at 25$^\circ$C, but they usually need of special synthesis conditions due to their high hygroscopicity. On the other hand, the high volatility of most of the components provokes difficulties to reproduce compositions.

Another approach which also yields promising results is the use of glass-ceramic electrolytes, i.e. materials with compositions of the systems Li₂O-Al₂O₃-GeO₂-P₂O₅ [10,11] or Li₂O-Al₂O₃-TiO₂-P₂O₅ [12]. Although they present a high chemical and thermal stability, the processing of the anode/glass-ceramic/cathode devices could be a source of additional problems such as complete elimination of mechanical stresses.

From the point of view of the chemical interaction between the electrode materials and electrolyte, the wettability of the glass to form stable interfaces is a crucial issue that glassy materials could best fulfil.
Lithium borophosphate glasses were first studied by Magistris et al. [13], who demonstrated that substitution of B$_2$O$_3$ for P$_2$O$_5$ leads to an increase in the room temperature ionic conductivity for a maximum ratio [B$_2$O$_3$]/([P$_2$O$_5$]+[B$_2$O$_3$]) of around 0.5. Other recent studies on the conductivity of Li$_2$O-B$_2$O$_3$-P$_2$O$_5$ glasses, with up to 0.47 molar fraction of Li$_2$O, has been focused on their possible application as thin-film solid electrolytes [14,15,16]. Cho et al. showed that the addition of P$_2$O$_5$ to lithium borate glasses decreases the room temperature conductivity with a maximum value of 1.6.10$^{-7}$ S.cm$^{-1}$ [15]. The authors interpreted the decrease in conductivity by the formation of four-fold coordinated boron atoms and the consequent decrease in BO$_3$ groups. This is, in fact, opposite to the assumption made by other authors that formation of the four-fold coordinated boron increase the conductivity because Li$^+$ ions become weaker linked to BO$_4$ than to BO$_3$ [17].

The purpose of this work has been to relate the behaviour of the properties of glasses with composition 50Li$_2$O.xB$_2$O$_3$.((50-x)P$_2$O$_5$, i.e. $T_g$, density, molar volume and ionic conductivity, with the B$_2$O$_3$ content as well as with the structure and microstructure of the glasses, which have been followed through X-Ray Diffraction, Nuclear Magnetic Resonance and Transmission Electron Microscopy.

2. Experimental

2.1 Glass melting

Lithium borophosphate glasses with composition 50Li$_2$O.xB$_2$O$_3$.((50-x)P$_2$O$_5$ (x = 2 to 25 mol %), have been obtained by conventional melt-quenching procedure. Reagent grade raw materials Li$_2$CO$_3$ (Aldrich, 99%), (NH$_4$)$_2$HPO$_4$ (Merck, 99%) and v-B$_2$O$_3$ (B$_2$O$_3$ previously melted at 800°C) were mixed in stoichiometric amounts and the batches were calcined in porcelain crucibles up to 450°C, in an electric furnace, and then melted
during 1 h at temperatures ranging from 800°C to 900°C depending on composition. The melts were poured onto brass moulds and annealed slightly above their glass transition temperature.

2.2 Characterisation of the glasses

Chemical analysis of the glasses was performed through Inductively Coupled Plasma-Emission Spectrometry ($\text{P}_2\text{O}_5$ and $\text{Al}_2\text{O}_3$) in a Thermo Jarrel Ash IRIS Advantage equipment, Flame Photometry ($\text{Li}_2\text{O}$) in a Perkin Elmer 2100 instrument and gravimetric and volumetric analysis to determine $\text{SiO}_2$ and $\text{B}_2\text{O}_3$ contents, respectively. Silica and alumina were determined for some glasses in order to check possible contamination from the crucible. A total amount of less than 1 wt. % for the sum of $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$ was found and then not relevant for the glass properties. The uncertainties of the chemical analyses were ±0.3 wt. %, 0.1 wt. % and 0.5 wt. % for $\text{Li}_2\text{O}$, $\text{B}_2\text{O}_3$ and $\text{P}_2\text{O}_5$, respectively, and the total error is taken as ±2 wt. %.

Glass transition temperature has been determined by Differential Thermal Analysis (DTA) in a SEIKO EXSTAR6000, TG-DTA6300, analyser using powdered samples in a platinum crucible, under static air and a constant heating rate of 10 K.min$^{-1}$. $T_g$ values are obtained at the onset of the endothermic effect of the DTA pattern and he estimated error in the determination of $T_g$ is assumed to be within ±2 K.

X-Ray Diffraction (XRD) analysis of the glasses was carried out with a D-5000 Siemens diffractometer using monochromatic Cu Kα radiation (1.5418 Å).

The density of the glasses was measured by helium pycnometry in a Quantachrome Corp. multipycnometer on bulk samples. The molar volume of the glasses ($V_m$) has been calculated from density measurements by using the relation $V_m = M/d$ (in cm$^3$.mol$^{-1}$), being $M$ the molecular mass, and $d$ the density of the glasses.
Transmission Electron Microscopy (TEM) was performed in a Hitachi H7100 using the carbon replica method. The samples were chemically etched with a 5 vol.% HF solution during 20 seconds.

Electrical conductivity measurements were performed by Electrochemical Impedance Spectroscopy (EIS) in a Gamry REF600 impedance analyser, within the frequency range from 10 Hz to 1 MHz at temperatures between 25 and 120°C, with an applied voltage of 0.5 V. The samples were cut into discs of 1–2 mm in thickness and ~10 mm in diameter and gold electrodes were sputtered on both faces as contacts for electrical measurements. The electrical conductivity (\(\sigma\)) is determined, for each temperature, through the resistance value (R) read at the low frequency intersection of the semicircle with the x-axis in the Nyquist plots and using the sample geometric factor (\(e/A\); \(e=\)thickness, \(A=\)electrode area) through the equation \(\sigma=e/(R\cdot A)\). The error in the determination of the conductivity is estimated to be less than 10%. The experimental data are then represented as a function of the reciprocal temperature and have been fitted to an Arrhenius equation of the type:

\[
\sigma = \sigma_0 \cdot \exp(-E_a/RT) \tag{1}
\]

where \(\sigma_0\) and \(R\) are the pre-exponential factor and gases constant, respectively, and \(E_a\) is the activation energy for conduction.

\(^{31}\)P MAS (Magic Angle Spinning) NMR (Nuclear Magnetic Resonance) spectra were recorded on a Bruker ASX 400 spectrometer operating at 161.96 MHz (9.4 T). The pulse length was 2.5 \(\mu\)s and 60 seconds delay time was used (sufficient to enable relaxation). A total number of 128 scans were accumulated with a spinning rate of 10 kHz. The \(^{31}\)P spectra were fitted to Gaussian functions, in accordance with the chemical shift distribution of the amorphous state [18]. The precision of the relative component
determination was ± 5%. Solid (NH₄)H₂PO₄ was used as secondary reference with a chemical shift 0.82 ppm with respect to H₃PO₄ (85%).

¹¹B MAS NMR spectra were recorded on a Bruker ASX 400 spectrometer operating at 128.38 MHz (9.4 T). The pulse length was 1.5 µs and 3 seconds delay time was used. A total number of 512 scans were accumulated under a spinning rate of 10 kHz. A solution of BF₃.Et₂O was used as reference.

³Li MAS NMR was performed on a Bruker ASX 400 spectrometer operating at 155.51 MHz (9.4 T). The pulse length was 2 µs and 2 seconds delay time was used. A total number of 256 scans were accumulated under a spinning rate of 10 kHz. Solid LiCl was used as secondary reference with chemical shift of -1.06 with respect to LiCl 1M solution.

3. Results

Table I shows the nominal and analysed compositions of the glasses as well as Al₂O₃ and SiO₂ contents for 50Li and 50Li10B samples, in mol %. All prepared glasses were homogeneous and transparent except 50Li25. This appeared with milky white aspect leading to opaque glass, suggesting that a liquid-liquid phase separation and/or crystallisation occurred. Glasses with higher than 25 mol % B₂O₃, i.e. 35, clearly crystallised after quenching. Figure 1 presents the XRD patterns of the 20, 25 and 35 mol % B₂O₃ containing samples. The XRD pattern of 50Li20B glass presents broad crystallisation peaks, clearly defined for further boron additions in 50Li25B and 50Li35B glasses, and identified as crystallisation of Li₃PO₄ (PDF file No. 15-0760).

Table II gathers the glass transition temperatures (Tᵥ), the density and molar volume (Vᵥm) and the activation energy for conduction (Eᵥa) of the borophosphate glasses.
Figure 2 depicts the variation of $T_g$ of the borophosphate glasses as a function of the boron oxide molar content. The glass transition temperature increases within the whole range of $B_2O_3$ contents, as already observed by Magistris et al. [13]. It shows an approximate linear behaviour between LiPO$_3$ (0 mol % $B_2O_3$) and 50Li20B glasses. This increase in $T_g$ is attributed to the increased cross-linking of the glass network between phosphate chains through P-O-B bonds, as will be shown hereafter.

Figure 3 presents the density and the molar volume of the glasses as a function of the $B_2O_3$ content. Glass density increases from 0 to 15 mol % $B_2O_3$, then it slightly decreases for higher boron contents. On the opposite, molar volume shows a continuous decrease between LiPO$_3$ and 50Li25B glass compositions. The decrease in molar volume indicates a higher reticulation of the glass network within the whole range of compositions, this being responsible for the increase of the glass transition temperature.

Figure 4 depicts the logarithm of the electrical conductivity as a function of the reciprocal absolute temperature for the 50Li$_2$O.x$B_2$O$_3$.($50$-$x$)P$_2$O$_5$ glasses. Activation energy for conduction (see Table II) decreases for $B_2O_3$ contents up to 20 mol %, remaining approximately constant within the error limits for further boron additions.

Figure 5 plots the Log of conductivity at 25°C, extrapolated from the Arrhenius fits, as a function of the $B_2O_3$ content in the glasses. The room temperature conductivity, Log $\sigma$$_{25^\circ}$C, increases with $B_2O_3$ up to 20 mol %, then slightly decreases for 50Li25B glass. Similar results have been observed by Magistris et al. [13], Cho et al. [15] and recently by Money et al. [19].

Figure 6 presents the $^{31}$P MAS NMR spectra of the 50Li$_2$O.x$B_2$O$_3$.($50$-$x$)P$_2$O$_5$ glasses from 2 to 25 mol % $B_2O_3$. For the 50Li2B glass, the decomposition of the spectrum needed three Gaussian bands at -4.4, -14.6 and -22.7 ppm. Phosphate glasses are built up of PO$_4$ tetrahedra, which are denominated $Q^n$ groups, as from Lippmaa et al.
definition [lippmaa], where n denotes the number of bridging oxygen atoms which are shared by two neighbouring phosphorous. In a metaphosphate glass, all phosphate groups are $Q^2$, having two bridging oxygens and two non-bridging equivalent ones, which gives rise to a network formed by long polymeric chains based on PO$_4$ tetrahedra. The decrease in the P$_2$O$_5$ content results in the formation of $Q^1$ (pyrophosphate) and $Q^0$ (orthophosphate) groups. The resonances at -4.4 and -22.7 are assigned to $Q^1$ and $Q^2$ sites [21], respectively, while the resonance at -14.55 ppm is identified as phosphorous atoms belonging to P-O-B bonds, which result from the substitution of B$_2$O$_3$ for P$_2$O$_5$ in the LiPO$_3$ glass, as already observed in borophosphate [22] and in P$_2$O$_5$-containing borosilicate glasses as well [23]. The increase in B$_2$O$_3$ content in the lithium borophosphate glasses leads to the increase in the intensity of the $Q^1$ and P-O-B groups and the decrease in the $Q^2$ phosphate units. A shift downfield of the three resonances is also observed with addition of B$_2$O$_3$ as already observed in phosphate glasses due to shortening of the phosphate chains. In addition, the $^{31}$P NMR spectra of the 20 and 25 mol % B$_2$O$_3$ glasses show a small but sharp peak at +9.5 ppm, which corresponds to crystallisation of Li$_3$PO$_4$ [24].

Figure 7 depicts the $^{11}$B MAS NMR spectra of the 50Li$_2$OxB$_2$O$_3$,(50-x)P$_2$O$_5$ glasses from 5 to 25 mol % B$_2$O$_3$. They show resonances typical for the presence of BO$_4$ as well as BO$_3$ groups for high boron-containing glasses. The BO$_4$ resonances exhibit Gaussian/Lorentzian lineshape, located at -3.4, -2.5 and -1.7 ppm that are attributed to B(OP)$_4$, B(OP)$_3$(OB) and B(OP)$_2$(OB)$_2$ species, respectively [22]. The BO$_4$ resonance at -3.4 ppm is observed for the glasses up to 10 mol % B$_2$O$_3$ with a small shift downfield with increasing boron content, but all the boron atoms remain four-fold coordinated in the glasses up to around 20 mol % B$_2$O$_3$. The broad resonance with a quadrupolar lineshape centred at ca. 15 ppm for B$_2$O$_3$ content ≥ 20 mol %, is assigned to trigonal
BO$_3$ groups [22]. The increase in the boron content is reflected in the increase in the amount of BO$_3$ trigonal groups respecting to BO$_4$ ones.

Tian et al. observed that for a constant 45 mol % Li$_2$O-containing glasses, N$_4$ (defined as the ratio between BO$_4$ groups and total amount of borate groups) first increases up to 15 mol % B$_2$O$_3$ then decreasing for further boron addition [17]. The results found in the present work show instead that a change in the coordination environment of boron atoms takes place at around 20 mol % B$_2$O$_3$. For a constant 50 mol % Li$_2$O composition, BO$_4$ units are the predominant species from 0 up to ~ 20 mol % B$_2$O$_3$, and then N$_4$ progressively decreases with further boron additions.

The $^7$Li MAS NMR spectra of the 50Li$_2$O.2B$_2$O$_3$.48P$_2$O$_5$ (50Li2B) and 50Li$_2$O.20B$_2$O$_3$.30P$_2$O$_5$ (50Li20B) glasses are shown in Fig. 8. They both present a single resonance centred at -0.75 ppm, but narrower for 50Li20B. It is characteristic to four-coordinated Li$^+$, as observed in LiPO$_3$ glass [25].

Figure 9 presents the TEM microphotographs of the glasses with 20 (a) and 25 (b) mol % B$_2$O$_3$, 50Li20B and 50Li25B, respectively. Glasses with compositions up to 15 mol % B$_2$O$_3$ were all homogenous. Small heterogeneities can be observed for borophosphate glass with 20 mol % B$_2$O$_3$ (Fig. 9a). 50Li25B glass (Fig. 9b) presented non-spherical defects resulting from the crystallisation of Li$_3$PO$_4$, as proved by XRD.

4. Discussion

The NMR results show two important structural features as the B$_2$O$_3$ content increases in the lithium borophosphate glasses:

i) P-O-B bonds are present at very low B$_2$O$_3$ content and their relative amount increases within the whole range of B$_2$O$_3$ contents.
ii) BO₄ tetrahedral borate groups are predominant, ~100%, up to 15 mol % B₂O₃. Then, proportion of BO₃ units increases.

In addition, ³¹P NMR spectra (Fig. 6) showed that the reticulation effect is accompanied by the formation of Q¹ terminal phosphate groups, or pyrophosphate ones, a sign of the phosphate network depolymerisation. However, Q¹ phosphate units might also be bonded to borate ones through P-O-B linkages, so that they cannot be considered as completely separated structural entities. The widening of the resonance bands does not allow to clearly distinguish how many, and in which proportion, the different types of phosphate species (Q² and Q¹ units) are bonded to either BO₃ or BO₄ boron groups. Therefore, a transition from a phosphate to a borophosphate glass network is expected to occur. Finally, the Q¹ phosphate units break down into Q⁰ sites that crystallise as Li₃PO₄, as shown by XRD for compositions with B₂O₃ ≥ 20 mol %.

As boron substitutes for phosphorous, the amount of P-O-B bonds increases and, from 20 mol % B₂O₃ glass, the BO₃ groups appear, giving rise to new linkages of the type B-(OP)₃ together with B-O-B ones.

From these structural considerations, the observed increase in Tg (Fig. 1) is attributed to the formation of both tetrahedral (BO₄) or trigonal (BO₃) groups linked to phosphate chains, that increase the network polymerisation through P-O-B bonds. The main reason for the increase in Tg comes from the reticulation produced by the P-O-B bonds which link together the phosphate chains. This effect is expected to be more important for BO₄ which form B-(OP)₃ linkages, than for BO₃ groups. Furthermore, the change in boron coordination, from BO₄ to BO₃, is also reflected in the decrease in density for boron contents higher than 15 mol %, though the molar volume of the glasses continuously decreases within the whole range of compositions. For glasses with 20 and 25 mol % B₂O₃, BO₃ trigonal units are clearly present in the structure of the glasses but, at the
same time, phase separation occurs and crystallization of Li$_3$PO$_4$. Phase separation as well as crystallisation might also play an important role contributing to alter the density of the samples for B$_2$O$_3$ contents higher than 20 mol % when those phenomena become more important, while the molar volume of the continues decreasing.

This structural model is also used to explain the behaviour of the room temperature conductivity of the glasses when B$_2$O$_3$ is introduced in lithium metaphosphate glasses. From 2 to 10 mol % B$_2$O$_3$, the Log of conductivity increases in an approximately linear manner, then showing a slower increasing rate between 10 and 20 mol % B$_2$O$_3$ (Fig. 5). The 50Li25B glass presents a lower Log $\sigma_{25^\circ C}$ than the one of 50Li20B. This conductivity behaviour may be separated within three different regions depending on the structural and microstructural features of the glass network observed:

**Region 1)** The increase in conductivity from 2 to 10 mol % B$_2$O$_3$ is due to the formation of B-(OP)$_4$ tetrahedra within a borophosphate glass network. Part of Li$^+$ ions behave as charge compensators of the BO$_4$ groups, thus increasing their mobility with respect to those in a pure phosphate network where all Li$^+$ behave as modifier ions.

**Region 2)** The lower increasing rate of conductivity from 10 to 20 mol % B$_2$O$_3$ is due to the decrease in the B-(OP)$_4$ bonds and the increase in the newly formed B-(OP,B)$_3$. Formation of trigonal BO$_3$ will contribute to decrease the amount of Li$^+$ as charge compensator, thus counteracting the increase in conductivity due to the BO$_4$ units. The higher the amount of BO$_3$ the lower the increase in conductivity.

**Region 3)** Decrease in conductivity for 25 mol % B$_2$O$_3$, due to Li$_3$PO$_4$ crystallisation. Lithium orthophosphate will block Li$^+$ ions as the crystalline phase is developed within the glass matrix. Crystallisation of Li$_3$PO$_4$ might also hinder mobility of Li$^+$ ions in 50Li20B and, for these higher B$_2$O$_3$ compositions, the phase separation
phenomenon producing a heterogeneous microstructure (see Fig. 9) is also responsible of a more difficult conduction through the sample.

Money et al. have recently reported the Log of conductivity at 110°C of 50Li2O.xB2O3.(50-x)P2O5 glasses as a function of the B2O3 content [19]. They attributed the increase in conductivity between 10 and 20 mol % B2O3 to BPO4 units which form new conduction pathway for lithium ions reducing the activation energy for ion migration. If BPO4 units were formed in borophosphate glasses, 31P NMR should show a resonance band at -30 ppm [26], which is actually not seen. Furthermore, in their study, Money et al. [19] proposed that the highest conductivity value observed for the 25 mol % B2O3 composition could be attributed to “a dispersion of Li3PO4 crystallites within the glass matrix”. The present work shows that Li3PO4 starts crystallising from 20 mol % B2O3, and the glass fully crystallises only for the 35 mol % B2O3 composition. For a 25 mol % B2O3 sample, there is strong phase separation (see Fig. 9), however, it is not easy to think on a continuous crystalline phase of Li3PO4. As discussed above, we can conclude that the increase in the conductivity of the lithium borophosphate glasses is specifically due to the new structural units formed in the glassy matrix through P-O-B bonds, which modify the bonding of Li+ ions as charge compensators in or tetrahedral BO3 unit, and not to Li3PO4 crystallites or BPO4 species. The non-linear change in properties observed for the lithium borophosphate glasses, such as density and Log σ25°C, resemble those provoked in alkali borate glasses due to the so-called boron anomaly [27]. Increasing alkali content leads to anomalous changes in the properties of the borate glasses, related to the transformation of BO3 groupings into BO4 ones. The non-linear behaviour observed in the properties takes place for the maximum amount of BO4 tetrahedra, which increase the reticulation of the glass network. In the present case, a continuous increasing of the B2O3 content produces a
modification of the glass properties while all the boron species are BO$_4$ units. Once BO$_4$ start to transform into BO$_3$ groups, the critical point in properties is attained (deviation density and Log $\sigma$ maxima), then showing a change in their linear behaviour. It is then worth mentioning it as a particular case of the boron anomaly.

**5. Conclusions**

A structure-properties relationship has been achieved for glasses of composition 50Li$_2$O.$x$B$_2$O$_3$.($1-x$)P$_2$O$_5$. The glasses were obtained transparent for B$_2$O$_3$ contents between 0 and 20 mol %. Glasses with B$_2$O$_3 > 20$ mol % presented crystallisation of Li$_3$PO$_4$, as well as phase separation, becoming fully crystallised in the case of 35 mol % B$_2$O$_3$.

The borophosphate glass network is built up of Q$^1$ and Q$^2$-type phosphate groups linked to BO$_4$ and BO$_3$ ones through P-O-B bonds. The higher the boron content the higher the P-O-B bonds and Q$^1$ phosphate groups. BO$_4$ tetrahedra are predominant up to 20 mol % B$_2$O$_3$. Addition of boron into lithium phosphate glasses gives rise to an increase in T$_g$ and decrease in the molar volume of the glasses, due to the increased reticulation of the network through the new P-O-B linkages formed. The room temperature conductivity of the glasses increases with boron addition up to 20 mol % B$_2$O$_3$ due to i) formation of BO$_4$ units, predominantly over BO$_3$ ones, which allow Li$^+$ ions behave as charge compensators; and ii) decrease of the Li-Li average distance through the decrease in molar volume. For $> 20$ mol % B$_2$O$_3$, ionic conduction is hindered as a consequence of the progressively increased amount of BO$_3$ borate units and, particularly, crystallisation of Li$_3$PO$_4$ and phase separation phenomena. The non-linear behaviour of the glass properties of lithium borophosphate glasses is interpreted in terms of a boron anomaly.
occurring when BO$_4$ tetrahedra transform into BO$_3$ groups after B$_2$O$_3$ substitutes for P$_2$O$_5$.

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References


Figure captions

Figure 1: X-ray diffraction patterns of the glasses with 20, 25 and 35 mol % B$_2$O$_3$, presenting crystallisation of Li$_3$PO$_4$.

Figure 2: Variation of the glass transition temperature of the borophosphate glasses as a function of the B$_2$O$_3$ content. Line is drawn as a guide for the eyes.

Figure 3: Density and molar volume ($V_m$) of the borophosphate glasses as a function of the B$_2$O$_3$ content. Lines are drawn as a guide for the eyes.

Figure 4: Log of conductivity for the 50Li$_2$O.xB$_2$O$_3$. (50-x)P$_2$O$_5$ glasses as a function of the reciprocal temperature. Experimental data points have been fitted to an Arrhenius type equation through the least squares method obtaining correlation coefficients of 0.998 (50LiPO$_3$), 0.999 (50Li2B), 0.999 (50Li5B), 0.999 (50Li10B), 0.999 (50Li15B), 0.999 (50Li20B) and 0.999 (50Li25B), from which Log $\sigma$ at 298 K and $E_a$ have been calculated.

Figure 5: Logarithm of conductivity at 298 K as a function of the molar percentage of B$_2$O$_3$ in the lithium borophosphate glasses. The values have been calculated by extrapolation using the Arrhenius fits in Fig. 4 at 298 K. The error bars are within the size of the symbol and line has been drawn as a guide for the eyes.

Figure 6 : $^{31}$P MAS NMR spectra of the 50Li$_2$O.xB$_2$O$_3$. (50-x)P$_2$O$_5$ glasses with x = 2 to 25 mol % B$_2$O$_3$.

Figure 7 : $^{11}$B MAS NMR spectra of 50Li$_2$O.xB$_2$O$_3$. (50-x)P$_2$O$_5$ glasses from x = 2 to 25 mol % B$_2$O$_3$.

Figure 8 : $^7$Li MAS NMR spectra of the glasses containing 2 and 20 mol % B$_2$O$_3$.

Figure 9: TEM microphotographs of the glasses with 20 and 25 mol % B$_2$O$_3$. 

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Table captions

Table I: Nominal an analysed compositions of the borophosphate glasses, in mol %.

Table II: Glass transition temperature ($T_g$), density, molar volume and activation energy for conduction ($E_a$) of lithium borophosphate glasses.

Figure 1
Figure 2
Figure 3
Figure 4
Figure 5

Log (σ in S cm⁻¹), 25°C
Figure 6
Figure 7
Figure 8
Figure 9
### Table I

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</tbody>
</table>

### Table II

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<tr>
<th>Glass</th>
<th>$T_g$ (± 2°C)</th>
<th>Density (± 0.01 g.cm$^{-3}$)</th>
<th>$V_m$ (cm$^3$.mol$^{-1}$)</th>
<th>$E_a$ (± 0.01 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50Li</td>
<td>311</td>
<td>2.34</td>
<td>36.6</td>
<td>0.83</td>
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<td>50Li2B</td>
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<td>36.2</td>
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<td>0.75</td>
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<td>50Li25B</td>
<td>n. d.*</td>
<td>2.41</td>
<td>28.2</td>
<td>0.67</td>
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</table>

*not determined.*