



Nitrogen and fluorine anionic substitution in lithium phosphate glasses

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ABSTRACT

Phosphate based glasses containing simultaneously fluorine and nitrogen in significant amounts have been prepared according to a new synthesis route described in this paper. The results obtained on glass series based on a $55\text{Li}_2\text{O} \cdot 45\text{P}_2\text{O}_5$ composition (mol %) allow, for the first time, the investigation of the effect of fluorine introduction on lithium phosphate and lithium phosphorous oxynitride glasses. New structural features, including the presence of an unreported fluorine site and a change in the Q^2 groups/fluorinated species ratio which depends on the lithium fluoride content, were derived from 1D ^{19}F and ^{31}P solid state NMR essays. Distinction between pure phosphate and fluorinated phosphate groups was established using the 2D $^{31}\text{P}\{^{19}\text{F}\}$ CP-HETCOR experiments. The evolution of the glass structure was studied as a function of the lithium fluoride content. The study of the properties of these glasses showed an increase of the ionic conductivity and a decrease of the glass transition temperature due to the phosphate network depolymerisation when lithium fluoride is introduced in the formulation.

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1. Introduction

During the last decades, phosphate glasses have gained much importance due to their properties which lead to many possible applications as matrices for vitrification of radioactive wastes [1], sealing elements in low temperature sealings [2] and matrices for generation of laser radiation [3]. The substitution and introduction of elements into the phosphate glasses may improve properties such as ionic conductivity [4–11], chemical durability [10,12–14] or thermal stability [14,15]. The improvement of these properties has also opened the possibility of the application of phosphate glasses as solid-state electrolytes in lithium rechargeable batteries [16–19]. A very well known reference is an amorphous thin film based on lithium phosphate with ionic conductivity of ca. $2 \cdot 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ suitable for application in lithium microbatteries [19]. This material, the so-called LiPON, was developed by Bates and co-workers [19]. The introduction of nitrogen during the preparation of LiPON thin films through Radio-Frequency Magnetron Sputtering under N_2 flow produces the increase of the ionic conductivity [19–22]. This increase has been proposed to be due to the decrease of electrostatic energy of LiPON with respect to the Li_3PO_4 reference material after the nitrogen/oxygen substitution [5], as well as by the increasing content of three-coordinated nitrogen species, N_t ($\text{P}-\text{N} < (\text{P})_2$), in the films [23].

Lithium phosphate glasses can be easily nitrated by ammonolysis [4,24], and it has been demonstrated that the oxygen by nitrogen substitution leads to the increase of the ionic conductivity [4–6], chemical

durability [12–14] or thermal stability [14]. During nitridation, two new structural units are formed as a consequence of the anionic network modification, the PO_3N and PO_2N_2 groups [5,25,26]. It has been proved that substitution of oxygen by nitrogen produces the increase of glass transition temperature due to an increase of the connectivity of the glass network by the formation of $\text{P}-\text{N}$ and $\text{P}=\text{N}$ bonds, which have higher covalent character compared to $\text{P}-\text{O}$ bonds [4]. Recently, Mascaraque et al. [6] confirmed that the observed increase on the ionic conductivity is due to the progressive increase of the non-bridging oxygens (NBO) content with nitrogen incorporation in the glasses with composition $x\text{Li}_2\text{O} \cdot (1-x)\text{P}_2\text{O}_5$ ($0.38 \leq x \leq 0.6$). Furthermore, it was observed that the lower the lithium content the higher is the increase of the conductivity produced by the introduction of nitrogen [6].

On the other hand, the addition of lithium fluoride leads to the depolymerisation of the phosphate network, producing the formation of $\text{P}-\text{F}$ and $\text{Li}-\text{F}$ bonds [11,27–29]. Respecting to the ionic conductivity of fluorine containing borate and phosphate glasses, literature presents two points of view. The first indicates that in fluoro-(phosphate, borate and aluminates) glasses [9,11,30–32], the conductivity increases with increasing fluorine content, due to a depolymerisation of the phosphate network that increases the mobility of lithium cations. However, other authors demonstrate that fluorine introduction produces the contrary effect, i.e. the decrease of ionic conductivity [33,34]; they argue that fluorine induces the creation of high potential energy network sites with strong cation–network interactions.

Independent of the effect of fluorine, it could be expected that nitridation of glasses containing fluorine will show an increased conductivity with respect to the non-nitrated glasses. This may justify the importance of obtaining glasses where both fluorine and nitrogen may

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coexist. Phosphate glasses in the system $\text{Al}_2\text{O}_3\text{--P}_2\text{O}_5\text{--MeF--AlN}$ (Me = Ba, Na) were prepared so far [35] using nitrides as the nitrogen source (AlN) with a maximum nitrogen content within the final glasses of only 0.72 wt.%. As well as silicate glasses $\text{Ca--Si--Al--O--N--F}$ [36] and $\text{Ca--(Y)--Si--Al--O--N--F}$ [37] which are prepared from Si_3N_4 by melting, and thin films of composition Si--O--N--F prepared by sol-gel [38].

The present work is focused on the preparation of lithium oxyfluoro-nitride glasses with high lithium contents and a suitable ionic conductivity for their application as solid electrolytes in lithium rechargeable batteries. An innovative synthesis process, consisting on a two-step melting process of a $\text{Li}_2\text{O--P}_2\text{O}_5$ glass, has been used to achieve the preparation of phosphate glasses allowing the incorporation of both fluorine and nitrogen at significant amounts. The evolution of the glass structure has been studied through 1D and 2D Nuclear Magnetic Resonance (NMR) techniques as a function of the LiF content, together with the effect of these changes in the properties, such as the ionic conductivity and glass transition temperature.

2. Experimental

2.1. Preparation of the oxyfluoride glasses by one-step process

Glasses belonging to the system of composition $(55 - x/2)\text{Li}_2\text{O} \cdot x\text{LiF} \cdot (45 - x/2)\text{P}_2\text{O}_5$ ($x = 10, 20, 25, 30$ mol%) were prepared by melt-quenching from batches of reagent grade materials Li_2CO_3 (99% ACS Reagent, Aldrich), $(\text{NH}_4)_2\text{HPO}_4$ (99% ACS Reagent, Merck) and LiF (99%, 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 800 °C. The glasses were obtained by pouring the melts onto a brass plate. In a separated process, the oxyfluoride glasses were nitrided by ammonolysis at 700 °C during different times. The ammonolysis [4,24] is a process based on the thermal treatment below 800 °C of the parent phosphate glass under ammonia flow. The glasses are put in graphite crucibles and treated in a tubular electric furnace where an ammonia flow passes during the nitridation time; finally the flow is changed by N_2 to prevent the oxidation of the glasses during cooling.

The chemical analysis reveals the total loss of fluorine (also confirmed by the lack of signal in the ^{19}F NMR analysis) during nitridation process. Thus, a new synthesis process has been designed that allows obtaining glasses where nitrogen and fluorine coexist with significant amounts within the glass.

2.2. Preparation of the fluorophosphate glasses by a two-step melting process

Glasses in the system $(55 - x/2)\text{Li}_2\text{O} \cdot x\text{LiF} \cdot (45 - x/2)\text{P}_2\text{O}_5$ ($x = 10, 20, 25, 30$ mol%) and called 10F, 20F, 25F, and 30F, were also prepared, through a two-step process. This process started from the parent glass $55\text{Li}_2\text{O} \cdot 45\text{P}_2\text{O}_5$, a lithium phosphate glass which has already been studied [6]. This glass was prepared by melt-quenching from batches of reagent grade materials Li_2CO_3 (99% ACS Reagent, Aldrich) and $(\text{NH}_4)_2\text{HPO}_4$ (99% ACS Reagent, Merck), calcined up to 400 °C during 1 day, and melted during 2 h at 850 °C. The glass was obtained by pouring the melt onto a brass mould.

Oxyfluoride glasses were prepared by re-melting the parent glass ($55\text{Li}_2\text{O} \cdot 45\text{P}_2\text{O}_5$) with reagent grade material LiF (99%, Merck). The batches were melted in porcelain crucible in an electrical furnace under nitrogen flow at 800 °C during 1 h and poured onto brass moulds.

As will be further shown, this process permits increasing the fluorine content in the resulting glasses.

2.3. Preparation of the oxynitride-fluoro-phosphate glasses by an innovative process

In this alternative process, firstly the parent glass ($55\text{Li}_2\text{O} \cdot 45\text{P}_2\text{O}_5$) was nitrided at 700 °C during 5 h and then re-melted with different

amounts of lithium fluoride to prepare oxyfluoronitride phosphate glasses in the system $(55 - x/2)\text{Li}_2\text{O} \cdot x\text{LiF} \cdot (45 - x/2)(\text{P}_2\text{O}_5\text{--PON})$ ($x = 10, 20, 25, 30$ mol%), and called 10FN, 20FN, 30FN and 40FN.

2.4. Characterisation of the glasses

X-ray powder diffraction (XRD) patterns were obtained in a Bruker D-8 diffractometer using monochromatic Cu K α radiation ($\lambda = 1.540598$) for 2θ from 10° to 70°.

Fluorine, lithium and phosphorus were analysed through selected electrodes, flame photometry and ICP-OES, respectively. The samples were previously dissolved in deionized water with 1 mL hydrochloric acid for determining the three elements.

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

$$\frac{N}{P} = \frac{M_{\text{base glass}} \cdot \text{wt.}\% \text{ N}}{10 + (140 + \text{wt.}\% \text{ N})} \quad (1)$$

where $M_{\text{base glass}}$ is the molecular mass of the glass without nitrogen and 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 glass transition temperature (T_g) was determined by Differential Thermal Analysis (DTA) in a SEIKO-6300 ATD/TG analyser, using a platinum crucible, at a constant heating rate of 10 °C \cdot min $^{-1}$, from 25 to 800 °C under air flow. Glass transition temperature (T_g) was determined at the onset of the endothermic effect shown in the DTA patterns, the error in T_g being within ± 5 °C.

Ionic conductivity measurements were performed using a VMP3 “BioLogic” electrochemical impedance analyser, in the frequency range from 10 Hz to 1 MHz at temperatures between 25 and 130 °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 sample's resistance (R) which is read at the intersection point with the horizontal axis. The conductivity is then calculated using the equation:

$$\sigma = \left(\frac{l}{R}\right) \cdot \left(\frac{l}{A}\right) \quad (3)$$

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

The ^{19}F and ^{31}P MAS NMR experiments have been performed at 376.7 and 162.9 MHz on a 400 MHz (9.4 T) Bruker spectrometer equipped with a HX 2.5 mm probe head operating at a spinning frequency of 20–25 kHz. It is noteworthy that the employed probe head allows for ^{19}F acquisition on the ^1H channel. The ^{19}F experiments have been recorded using a 2 μs pulse length (90° pulse), a 125 kHz radio-frequency field (rf) strength, 512 accumulations and a recycle delay (rd) of 30 s. Solid Na_2SiF_6 was used as secondary reference with chemical shift of -152.46 ppm with respect to CFCl_3 . The ^{31}P experiments have been acquired using a 3 μs pulse length (90°), a 80 kHz radio-frequency field (rf) strength, 16 accumulations and a recycle delay (rd) of 60 s. The chemical shifts were referred to H_3PO_4 as 0 ppm. The spatial proximity between the fluorine and phosphate species was investigated using the two-dimensional (2D) Cross Polarization HETeronuclear CORrelation (CP-HETCOR) technique. This sequence uses a distance dependent magnetization transfer from ^{19}F to ^{31}P to edit 2D NMR spectra where the P/F spatial proximity is highlighted through a correlation signal. The 994×64 acquisition points have been recorded at a spinning frequency of 20 kHz using a 10 μs F1 increment time. Each F2 slice has been recorded with 64 accumulations and an rd of 30 s. The magnetization transfer has been achieved during 3 ms by simultaneously irradiating the ^{19}F and ^{31}P nuclei

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