Synthesis and characterisation of SnO-containing phosphorous oxynitride glasses

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Abstract

SnO-containing oxynitride phosphate glasses have been obtained by ammonolysis and their structure studied by Nuclear Magnetic Resonance. The nitried glasses are characterised by tetrahedral units P(O,N)₄ in which nitrogen atoms have substituted both bridging and non-bridging oxygen atoms. The N/O substitution in the anionic network induces important changes in the glass properties such as an increase in the glass transition temperature and a decrease in the coefficient of thermal expansion. ³¹P MAS NMR shows that PO₄, PO₃N and PO₂N₂ units coexist within the vitreous network and their relative proportions are a function of the nitrogen content as well as of the base glass composition. The influence of the different modifiers on the nitridation process is explained through a comparative study of the LiNaSnPON and LiNaPbPON systems. Unlike lead in oxynitride glasses, tin affects the nitridation mechanism by limiting the nitrogen/oxygen substitution in the anionic network, so that the substitution model is assumed to be closer to the one taking place in alkali phosphate glasses LiNaPON.

Keywords: Nitrided Phosphate Glasses; Nitridation; Sealing Glasses; SnO; Structure; Nuclear Magnetic Resonance
1. Introduction

Phosphate glasses generally present low characteristic temperatures, i.e. glass transition \((T_g)\) and dilatometric softening temperature \((T_d)\), and high Coefficient of Thermal Expansion \((CTE)\) which make them suitable for low temperature sealing applications. Nevertheless, they present a poor chemical durability that limits their use. The addition of oxides in the vitreous matrix such as PbO, Al\(_2\)O\(_3\) or Fe\(_2\)O\(_3\) improves the durability [1,2], but there is also a significant influence on the thermal properties. The compromise research between good chemical durability and lower characteristic temperatures is an important issue. Nitridation, consisting in the substitution of nitrogen for oxygen, seems to be an efficient way to improve the chemical durability [3-8] due to the lower change of the thermal characteristics.

It has been proved by \(^{31}\)P Nuclear Magnetic Resonance (NMR) that nitridation of phosphate glasses leads to the formation of oxynitride tetrahedra, PO\(_3\)N and PO\(_2\)N\(_2\) [9-12]. On the other hand, X-ray Photoelectron Spectroscopy (XPS) results have shown that nitrogen may exist as two-coordinated –\(\text{N}=\) (Nd) and three-coordinated –\(\text{N}<\) (Nt) species bonded to two and three phosphorous atoms, respectively [9,10]. The nitridation of phosphate glasses increases the bonding density, which is the responsible for the modification of the physico-chemical properties.

The special thermal and rheological properties of lead phosphate glasses make them suitable materials for sealing applications. However, lead oxide is associated with deleterious health and environmental effects [13]. Furthermore, PbO-containing oxynitride phosphate glasses have already been studied by Pascual et al. [7,14] and Muñoz et al. [8,11] and due to their interesting properties and the noticeable increase in the chemical durability after nitridation, one may think on their possibilities of application.
In the present work, SnO has been chosen as a substitute of lead in order to prepare suitable glasses with similar properties for future applications. The aim of the work has been to report a study on the synthesis and characterization of tin-containing phosphorous oxynitride glasses with composition Li_{0.25}Na_{0.25}Sn_{0.25}PO_{3-3x/2}N_x (0<x≤0.52). Nuclear Magnetic Resonance (NMR) is applied to follow the structural evolution as nitrogen is incorporated into the glass network. Besides the importance of using SnO from the point of view of the potential applications of the glasses as low-temperature seals, the mixed-alkali metaphosphate glass composition has been chosen to be compared with the previously studied systems Li_{0.5}Na_{0.5}PO_{3-3x/2}N_x and Li_{0.25}Na_{0.25}Pb_{0.25}PO_{3-3x/2}N_x systems [11,12].

2. Experimental

2.1 Glass synthesis

The base metaphosphate glass of composition Li_{0.25}Na_{0.25}Sn_{0.25}PO_3 was prepared by melting reagent grade Li_2CO_3 (Acros, 99%), Na_2CO_3 (Aldrich, 99.5%), SnO (Aldrich, 99+%) and H_3PO_4 (Aldrich, 85 wt.%; d=1.7 g cm^{-3}) in an electric furnace. The batch was first calcined in a porcelain crucible up to 450°C for 24 h and then melted at 1000°C for 1 h. The melt was quenched in air onto a brass mould and then annealed for 30 min above the glass transition temperature. The glass was clear, colourless and bubble free.

Tin-containing phosphorous oxynitride glasses Li_{0.25}Na_{0.25}Sn_{0.25}PO_{3-3x/2}N_x (LiNaSnPON) were prepared by thermal treatment of the base oxide glass under anhydrous ammonia flow (15 l h^{-1}) at temperatures ranging from 600 to 750°C and times up to 30 h. For each nitridation treatment, about 0.5 g of the base oxide glass were placed in a graphite crucible and placed into a gas-tight Al_2O_3 tube furnace (850 cm^3 in volume) and flushed with dry nitrogen to remove air. The furnace was heated up to the nitridation temperature, and then nitrogen was replaced by a constant flow of anhydrous ammonia. At the end of the thermal
treatment, the ammonia flow was switched to nitrogen and the furnace was allowed to cool down to room temperature.

2.2 Glass characterisation

Nitrogen analyses were carried out in a nitrogen/oxygen LECO-TC436 analyser. The N/P ratio is expressed by the $x$ value in the glass formulation Li$_{0.25}$Na$_{0.25}$Sn$_{0.25}$PO$_{3-3x/2}$N$_x$. The incertitude in the determination of the N/P ratio was ±0.02.

Glass transition temperatures ($T_g$) have been determined by Differential Thermal Analysis (DTA) and performed in a TA Instruments Model SDT 2960 analyser using a Pt crucible in air. The precision of the instrument is within ±2°C. The Coefficients of Thermal Expansion (CTE) were determined by Thermomechanical Analysis in a TA Instruments Model TMA 2940, using a 2 K min$^{-1}$ heating rate and a preload force of 0.1 N. The precision in the CTE determination is ±2.10$^{-7}$ K$^{-1}$.

Solid state NMR experiments were performed with a BRUKER “AVANCE 300” spectrometer operating at 7 Tesla for the static magnetic field $B_0$. The $^{31}$P Magic Angle Spinning (MAS) NMR spectra were obtained under a resonance frequency of 121.53 MHz and a $\pi/2$ pulse, 2 $\mu$s, and 5 s recycle delay were applied. The short recycle delay time was verified to be enough to allow relaxation and quantification. In particular, $^{31}$P MAS NMR experiments in Sn-containing glasses have already been performed by using such a short recycle delay times [15]. The spinning rate was 15 kHz and a total of 256 scans were accumulated for every spectrum. H$_3$PO$_4$ (85%) was used as the reference. The decomposition of the spectra was carried out by means of the *dmfit* software [16] and the precision of the relative component estimation was ±5%.
3. Results

3.1 Nitridation kinetics and thermal properties

Figure 1 plots the progressive nitrogen enrichment (expressed as the atomic N/P ratio) in LiNaSnPON and Li\(_{0.25}\)Na\(_{0.25}\)Pb\(_{0.25}\)PO\(_{3-3x/2}\)N\(_x\) (LiNaPbPON) glasses as a function of the reaction time in flowing ammonia at 700°C. Data for LiNaPbPON glasses are provided by Muñoz et al. [see ref. 11]. Nitridation kinetic curves show a rapid increase of the nitrogen content for short treatment times, reaching an asymptotic limit around 10 h for LiNaPbPON glasses and 20 h for LiNaSnPON ones. The maximum N/P ratio has been found to be 0.52 for LiNaSnPON glasses and 0.69 for LiNaPbPON ones.

Figure 2 depicts the variation of the nitrogen content as a function of the treatment temperature, for a constant time of 3 h, in both tin and lead oxynitride glasses. The nitrogen content for both systems increases proportionally to the treatment temperature. Below 700°C, the nitrogen content is higher for LiNaSnPON glasses while it becomes lower than for lead glasses from 700°C, so that the slope of the variation of N/P ratio with temperature may be considered bigger for LiNaPbPON glasses.

Figure 3 shows the variation of the \(T_g\) as a function of the nitrogen content for LiNaSnPON glasses. Glass transition temperature increases linearly with N/P ratio, which is due to the increase in the glass network reticulation and the higher covalence of the P-N and P=N bonds of the P(O,N)\(_4\) tetrahedra with respect to the P-O bonds.

Figure 4 displays the variation of the Coefficient of Thermal Expansion as a function of the N/P ratio in the LiNaSnPON glasses. CTE decreases with nitrogen content for N/P ratio up to 0.26, with no further modification for higher nitrogen contents.

3.2 \(^{31}\)P Nuclear Magnetic Resonance
$^{31}$P MAS NMR spectra of Li$_{0.25}$Na$_{0.25}$Sn$_{0.25}$PO$_{3.3x/2}$N$_x$ (0<x<0.52) glasses are depicted in Fig.5. The oxide base glass (x=0) shows a main resonance at -25.1 ppm which is attributed to Q$^2$-type sites [17]. The value of the chemical shift is lower than the ones found in LiNaPO$_3$ (-21.4 ppm) [12] and LiNaPbPO$_3$ (-23 ppm) [11] glasses. The chemical shift is a function of the Ionic Field Strength (I.F.S.), $z/r^2$, where $z$ is the cation charge and $r$ the ionic radius [18]. The higher the I.F.S of the modifier cations the higher the shielding effect over the $^{31}$P chemical shift. Whereas cations Li$^+$, Na$^+$ and Pb$^{2+}$ have a ionic field strength value of 0.23, 0.19 and 0.28, respectively, Sn$^{2+}$ presents the higher value, 0.33 [18]. The spectrum shows also another resonance band at -13 ppm, which is assigned to a small amount of Q$^1$-type sites in accordance with Brow et al. [19], and indicates a small deviation from the metaphosphate composition. As the N/P ratio increases, the width of the spectra increase and the positions of the peak maximums move towards more positive chemical shift values, indicating reduced shielding of the phosphorous nucleus. Fig. 6 depicts an example of the decomposition of the $^{31}$P NMR spectrum for the oxynitride Li$_{0.25}$Na$_{0.25}$Sn$_{0.25}$PO$_{2.22}$N$_{0.52}$ glass. The inset picture in Fig. 6 shows the complete spectrum including the spinning side bands. The decomposition of the spectra of oxynitride glasses requires three components [3,6,11], which for the composition with x=0.52 are located at chemical shifts of -22, -11 and -5 ppm and assigned to PO$_4$, PO$_3$N and PO$_2$N$_2$ tetrahedra, respectively. With increasing nitrogen content, the resonance bands of the P(O,N)$_4$ groups are shifted to higher chemical shifts due to the deshielding effect of shorter phosphate chains in which these groups are involved [11]. Thus, it can be noted an increase in the chemical shifts towards more positive values between the oxide base glass and the oxynitride one (N/P=0.52), from -25 to -22 ppm, -12 to -11 ppm and -6 to -5 ppm, assigned to PO$_4$, PO$_3$N and PO$_2$N$_2$ tetrahedra, respectively.

The resonance bands of the Q$^1$-type sites and of the PO$_3$N units appear at a very similar chemical shift and it is difficult to separate both components. As it has also been done
in previous works [11, 12], the proportion of $Q^1$ groups is not taken into account for the decomposition of the spectra since as nitrogen increases, $Q^1$ groups are supposed to be transformed into $PO_3N$ and $PO_2N_2$ ones too. Therefore, the total contribution of $Q^1 PO_4$ tetrahedra to the whole spectrum will be minimised with nitrogen incorporation.

Figure 7 displays the relative proportions of the three types of $P(O,N)_4$ tetrahedra as a function of the N/P ratio. The proportion of $PO_4$ tetrahedra decreases with the N/P ratio down to a value of 33%. The proportion of $PO_3N$ units shows a fast increase with increasing N/P, then it remains approximately constant from $x=0.25$ (33% of $PO_3N$ units) though it tends to slightly decrease from $x=0.36$. The proportion of the $PO_2N_2$ units slowly increases up to $x=0.25$ in a first step, then it presents a more significant increase at the same time that the $PO_3N$ proportion remains nearly constant.

Figures 8(a), 8(b) and 8(c) make the comparison of the variation of the $PO_4$, $PO_3N$ and $PO_2N_2$ proportions, respectively, as a function of the N/P ratio in both LiNaSnPON and LiNaPbPON oxynitride glasses. The proportion of the $PO_4$ groups decreases similarly for both systems. On the other hand, $PO_3N$ and $PO_2N_2$ units in LiNaSnPON glasses are lower and higher, respectively, than in LiNaSnPON glasses. This difference will be explained below through the different role of tin and lead over the nitridation mechanism.

4. Discussion

The influence of the glass composition on the nitridation kinetics as well as on the behaviour with temperature is studied from the results of Fig. 1 and 2. Meanwhile the nitridation rate seems to be not very different after the first 3 hours of treatment, the nitrogen incorporation rate becomes lower for the LiNaSnPON glasses, from 5 h treatment, and the value of the maximum N/P ratio reached is lower than in LiNaPbPON as indicated above. The initial rate of nitrogen incorporation has been proved to be greatly depending on the viscosity
of the base glass at the nitridation temperature [20]; the lowest the base glass viscosity the fastest the nitridation rate. Even though there is not available data on viscosity for the Li$_2$O-Na$_2$O-SnO-P$_2$O$_5$ system and, especially for the oxynitride glasses, the fact that the nitrogen incorporation rate in LiNaSnPON glasses is lower than for the LiNaPbPON ones might be determined by a higher viscosity of the tin-containing base glass at the nitridation temperature of 700ºC. At the same time, maximum N/P ratio will depend not only on structural reasons but also on viscosity of the oxynitride glasses. It has also been demonstrated that viscosity increases with nitrogen content [6]. Thus, when the oxynitride composition reaches a certain nitrogen content, for which the viscosity has attained the value above which there is no further nitrogen incorporation possible, the nitrogen/oxygen substitution may be stopped and this nitrogen content is kept constant even for longer treatment times.

On the other hand, Fig. 2 shows a similar increase of N/P ratio with treatment temperature for a constant time in both Sn and Pb oxynitride glasses. The most important difference is the bigger slope of the increase of N/P ratio with T in the LiNaPbPON glasses, which could also be due to lower viscosity values of the LiNaPbPON glasses for T>700ºC and, therefore, higher nitrogen incorporation.

The glass transition temperature increases linearly with the nitrogen content (Fig. 3), which confirms that $T_g$ depends on the strength and the number of P-N and P=N bonds created [6,21]. The increase in the glass transition temperature is approximately 30% for N/P=0.5. The same behaviour was observed in previous oxynitride glass systems, such as LiNaPON [12] and LiNaPbPON [11]. The Coefficient of Thermal Expansion decreases with increasing nitrogen content (Fig. 4). In a first step, between N/P=0 and N/P~0.25, there is a decrease with N/P ratio, as it occurs generally in oxynitride glasses [6,8,21]. It is known that the thermal expansion depends on the number of bridging oxygen atoms and the bond strength between oxygen atoms and former (and/or modifier) cations. The N/O substitution
leads to the formation of new cross-links between the phosphate chains, thus explaining the decrease in the CTE. Nevertheless, for N/P ratios above 0.25 in LiNaSnPON, CTE remains constant despite further incorporation of nitrogen into the glass network. An associated structural change may also be taking place that would counteract the decrease in the CTE due to the increased glass network reticulation, so that the resulting effect makes the CTE to remain constant without any further change. In this case, there is no previous evidence of a similar behaviour of CTE in nitrided glasses, so a comparison with other systems can not be made and more data would be needed to reach a proper explanation.

From the structural characterisation carried out by $^{31}$P NMR and the evolution of the different P(O,N)$_4$ structural units coexisting into the glass network of both Sn and Pb-containing systems, the following remarks can be pointed out:

i) The variation of the PO$_4$ units is quite similar for the two systems, both showing a regular decrease of PO$_4$ with increasing nitrogen.

ii) The initial rate of formation of PO$_3$N units is slower for LiNaSnPON as well as the maximum proportion reached. From N/P=0.36, the percentage of PO$_3$N units tends to slightly decrease, though it can be considered to be constant within the limits of error.

iii) On the opposite, the rate of formation of PO$_2$N$_2$ units is faster in LiNaSnPON glasses and the maximum value reached is higher.

Le Sauze et al. described the nitridation mechanism in Li$_{0.5}$Na$_{0.5}$PO$_3$ glasses by the progressively growing of oxynitride microdomains at the expense of the oxide regions [12]. The N/O substitution takes place in a random way for very low nitrogen contents and oxide and oxynitride domains coexist homogeneously distributed. After further N/O substitution, PO$_2$N$_2$ tetrahedra appear by substituting preferentially the bridging oxygen atoms shared by a PO$_4$ tetrahedron and a PO$_3$N one. The authors also concluded that non-bridging oxygens
coordinating modifier cations are not substituted [12]. In the case of the LiNaPbPON glasses, the nitridation does not take place randomly even since the very beginning [11]. However, the Pb$^{2+}$ ions are supposed to induce a first N/O substitution in all the PO$_4$ tetrahedra surrounding lead atoms, thus giving rise only to PO$_3$N tetrahedra before formation of PO$_2$N$_2$ tetrahedra.

In the present case of Sn-containing oxynitride glasses, the proportion of the PO$_3$N groups is lower than in the lead glasses, for all nitrogen contents, and the one of PO$_2$N$_2$ groups higher. The comparison between both tin and lead systems, together with LiNaPON and NaPON glasses, allows to see that the behaviour of P(O,N)$_4$ tetrahedra in LiNaSnPON glasses may be placed in between the LiNaPbPON system and the pure alkali ones. Unlike LiNaPbPON glasses, PO$_3$N and PO$_2$N$_2$ groups already coexist inside the glass network even for the lowest nitrogen contents as it occurs in oxynitride alkali glasses [12]. Therefore, the mechanism of nitridation in LiNaSnPON glasses is supposed to be closer to the one taking place in LiNaPON system. The study about the tin ions environment by NMR and Mössbauer spectroscopy will help in the explanation of the nitrogen/oxygen substitution mechanism through possible structural changes taking place during nitrogen incorporation, which is already on progress. On the other hand, further research efforts are currently being made to complete the work initiated here, in particular, for determining the viscosity of the Sn-containing glasses as well as of the oxynitride compositions in order to get insight about the nitridation kinetics.

5. Conclusions

The Li$_{0.25}$Na$_{0.25}$Sn$_{0.25}$PO$_3$ glass has been nitrided by heat treatment in ammonia flow up to the Li$_{0.25}$Na$_{0.25}$Sn$_{0.25}$PO$_{2.22}$N$_{0.52}$ composition. The N/P ratio, which increases with the treatment temperature, tends towards an upper limit. The glass transition temperature increases whereas the coefficient of thermal expansion decreases with the nitrogen content.
resulting from the network reticulation. The $^{31}$P MAS NMR shows that the oxynitride glasses are composed of PO$_4$, PO$_3$N and PO$_2$N$_2$ coexisting tetrahedral units. The nitridation mechanism in tin-containing glasses is closer to the one observed in LiNaPON glasses. It takes place in an initial random N/O substitution followed by a progressive growing of nitride microdomains from oxide ones. Compared to lead-containing glasses, it is clear that divalent tin ions limit the introduction of nitrogen in the anionic network. But the influence of Sn$^{4+}$, contained in the oxide base glass, is not yet well understood. Further experiments of NMR and Mössbauer spectroscopy will be performed and used to study the evolution of the Sn$^{4+}$ content in the oxynitride glasses and its role on the nitridation mechanism.

**Acknowledgements**

This work has been supported by a research grant from the French Ministry of Research and Education. F. Muñoz thanks his present I3P contract from CSIC (Spain) associated to the project CICYT-MAT2006-4375 of the Spanish National Materials Programme.
References


**Figure captions**

Figure 1: Variation of the N/P ratio of LiNaSnPON and LiNaPbPON glasses as a function of the treatment time in flowing ammonia at a constant temperature of 700°C. The lines are drawn as a guide to the eyes.

Figure 2: Variation of the N/P ratio of LiNaSnPON and LiNaPbPON glasses as a function of the treatment temperature in flowing ammonia for a constant time of 3 hours. The lines are drawn as a guide to the eyes.

Figure 3: Variation of the glass transition temperature as a function of the N/P ratio of LiNaSnPON glasses.

Figure 4: Coefficient of thermal expansion as a function of the N/P ratio of LiNaSnPON glasses.

Figure 5: $^{31}$P MAS NMR spectra of Li$_{0.25}$Na$_{0.25}$Sn$_{0.25}$PO$_{3-3x/2}$N$_x$ ($0 < x \leq 0.52$).

Figure 6: Decomposition with DMFIT software of the main resonance band in the $^{31}$P NMR spectrum for the Li$_{0.25}$Na$_{0.25}$Sn$_{0.25}$PO$_{2.22}$N$_{0.52}$ oxynitride glass. Solid line: experimental spectrum; dashed line: calculated spectrum; dotted lines: individual components. The inset figure shows the complete spectrum including spinning side bands.

Figure 7: Relative proportions of PO$_4$, PO$_3$N and PO$_2$N$_2$ tetrahedra as a function of the N/P ratio in LiNaSnPON glasses. The lines are drawn as a guide to the eyes.

Figure 8: Relative proportions of P(O,N)$_4$ units as a function of the N/P ratio in LiNaSnPON and LiNaPbPON glasses: PO$_4$ (a), PO$_3$N (b) and PO$_2$N$_2$ (c) tetrahedra. The lines are drawn as a guide to the eyes.
Figure 2
Figure 3
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Figure 5
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Figure 7
Figure 8