

# Oxidation behaviour of Li–Na–Pb–P–O–N oxynitride phosphate glasses

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## Abstract

The oxidation behaviour of different oxynitride phosphate glasses, elaborated by thermal ammonolysis of oxide base glasses with composition  $(25 - x/2)\text{Li}_2\text{O} \cdot (25 - x/2)\text{Na}_2\text{O} \cdot x\text{PbO} \cdot 50\text{P}_2\text{O}_5$  ( $0 < x < 50$ ), has been studied in air by thermogravimetric analysis and differential scanning calorimetry. The oxidation of the nitrated powders proceeds first from a surface oxidation, followed by a bulk oxidation controlled by diffusion. As the nitrogen content increases, the sintering becomes slower and the surface oxidation is greater. The second step, which depends on the particular composition, takes place once the glass viscosity has decreased enough to allow oxygen diffusion inside the glass particles.

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## 1. Introduction

Phosphate glasses have specific properties such as low glass transition and dilatometric softening temperatures, a high thermal expansion coefficient or UV transparency. These properties make them interesting for applications as low-temperature sealing materials,<sup>1–6</sup> vitrification of nuclear wastes,<sup>7,8</sup> as well as laser host matrices when doped with rare-earth elements.<sup>9–12</sup> However, their low chemical durability is a drawback which can limit their practical use.

Partial substitution of nitrogen for oxygen is one of the most effective ways to improve the chemical resistance of phosphate glasses. Since the first nitrated experiments reported by Marchand<sup>13</sup> and Wilder et al.<sup>14</sup> as early as 1983, many compositions have been studied from both fundamental and application viewpoints.

The higher bonding density generated by nitrogen rather than oxygen atoms along with the greater covalent character of P–N bonds compared to P–O bonds result in a greater toughness of the glass network with respect to corresponding

oxide glasses. The consequence is that nitrogen incorporation produces an increase in the glass density, glass transition and softening temperatures, viscosity, hardness and mechanical properties, refractive index, electrical resistivity, as well as in the chemical durability.<sup>15–22</sup> In addition, nitrated glasses are more stable towards crystallization than corresponding oxide glasses.

Oxynitride phosphate glasses are commonly prepared by thermal ammonolysis of parent oxide glasses at temperatures ranging from 600 to 800 °C. Nitrogen atoms substitute for both bridging and non-bridging oxygens of the PO<sub>4</sub> tetrahedra network. Nuclear magnetic resonance has evidenced formation of two new structural units, the PO<sub>3</sub>N and PO<sub>2</sub>N<sub>2</sub> tetrahedra,<sup>23–26</sup> in which the nitrogen atoms are coordinated to two phosphorous, –N=(N<sub>d</sub>), or to three phosphorous, –N<(N<sub>t</sub>), as shown by X-ray photoelectron spectroscopy.<sup>26,27</sup>

The presence of glassy phases in the grain boundaries of silicon nitride-based ceramics has led to study the formation conditions of such glass compositions and their properties as a function of the nitrogen content. At the same time, owing to a context of high temperature applications, systematic studies of the oxidation resistance of these SiAlON glasses have been carried out.<sup>28,29</sup>

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On the other hand, even though the structure and properties of oxynitride phosphate glasses have been widely studied, no references concern their oxidation behaviour. The application of oxynitride phosphate glasses as sealing materials requires the stability of the glass during the sealing process. The present work constitutes a first study of the behaviour of such glasses in an oxygenated environment. The oxidation behaviour in air of Li–Na–Pb–P–O–N oxynitride glasses has been studied by thermo gravimetric analysis (TG) and differential scanning calorimetry (DSC). The influence of the nitrogen content, the composition of the oxide base glass, and the particle size of the powdered glass samples have been particularly investigated.

## 2. Experimental

Metaphosphate glass compositions  $(25 - x/2)\text{Li}_2\text{O} \cdot (25 - x/2)\text{Na}_2\text{O} \cdot x\text{PbO} \cdot 50\text{P}_2\text{O}_5$  ( $0 < x < 50$ ), in mol%, were prepared from stoichiometric amounts of reagent grade  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Pb}_3\text{O}_4$  and  $\text{H}_3\text{PO}_4$  (85 wt.%,  $d = 1.71 \text{ g cm}^{-3}$ ) in a gas furnace. The batches were first calcined up to  $450^\circ\text{C}$  in porcelain crucibles for 1 week, and then melted at  $1100^\circ\text{C}$  for 1 h. The melts were poured in air over brass plates, after that the glasses were annealed for 30 min in an electrical furnace slightly above their glass transition temperatures. All the base glasses were clear, colourless and bubble-free.

Nitridation was carried out by thermal treatment of the base glasses under anhydrous ammonia flow ( $< 400$  ppm  $\text{H}_2\text{O}$ ). The base glasses were crushed in dry conditions using an agate mortar up to glass particle size of about 1 mm. The powdered glass samples were heated between  $600$  and  $750^\circ\text{C}$  for times between 1 and 30 h in a gas-tight  $\text{Al}_2\text{O}_3$  tube furnace of 120 cm in length and 7.5 cm in diameter. A constant heating rate of  $5^\circ\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere was applied up to the treatment temperature, at this point nitrogen was replaced by a constant ammonia flow of  $500 \text{ cm}^3 \text{ min}^{-1}$ , and finally the cooling stage down to room temperature was again under  $\text{N}_2$ . All the oxide and oxynitride glass samples were examined and confirmed to be X-ray amorphous.

The nitrogen determination was carried out in a  $\text{N}_2/\text{O}_2$  analyzer *LECO TC-436*. At least three analyses were done for each sample using identical condition with an average  $\sigma_{n-1} = 0.02$ . The nitrogen content is given as

the atomic N/P ratio according to the glass formulation  $(\text{LiNaPb})\text{PO}_{3-3x/2}\text{N}_x$ .

The coefficient of thermal expansion (CTE), glass transition ( $T_g$ ) and dilatometric softening ( $T_s$ ) temperatures were determined from the thermal expansion curves obtained in air with a *Netzsch Gerätebau* dilatometer, model 402 EP, at a heating rate of  $2 \text{ K min}^{-1}$ . For measurements, prismatic samples, of around 10 mm length between the two parallel faces in contact with the dilatometer, were prepared by cutting and polishing from the base and nitrated glasses.

The oxidation studies were carried out in a TA instruments SDT 2960 simultaneous DSC-TGA analyzer, using powdered glass samples with three particle size distributions ranging from 38 to 63  $\mu\text{m}$ , 63 to 100  $\mu\text{m}$  and 100 to 200  $\mu\text{m}$ . Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) experiments were performed under static air in platinum crucibles with a constant weight sample ( $30 \pm 0.1 \text{ mg}$ ) and a constant heating rate of  $10^\circ\text{C min}^{-1}$ , which was proved to be appropriate for such a study. Temperature calibration was carried out over a large range employing high purity materials improved by the International Committee for Thermal Analysis (ICTA). The overall accuracy of this instrument is expected to be better than  $1.5^\circ\text{C}$ .

## 3. Results and discussion

Table 1 gathers the main thermal properties of some of the oxide and oxynitride glass compositions considered in this study, which are crucial information for their application as sealing glasses: the glass transition and dilatometric softening temperatures, and the thermal expansion coefficient. The maximum temperature to be used during the sealing process can be estimated reasonably as not higher than  $T_s + 100^\circ\text{C}$ . So, using oxynitride compositions, the temperature would not reach a limit of  $500^\circ\text{C}$ .

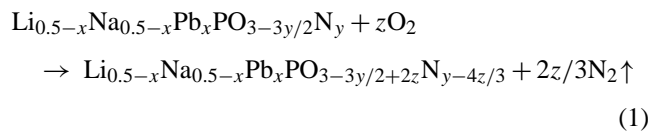
When heated in an oxygenated atmosphere, nitride-type compounds are systematically transformed, at relatively high temperature, into oxides – or a mixture of oxides – with release of molecular nitrogen. In the present case, the thermal treatment of oxynitride phosphate glasses in an oxygen-containing atmosphere should finally result in their transformation into the corresponding initial base glasses. So, considering the initial and final stages, the oxidation is the opposite of the ammonolysis. For a glass composition

Table 1

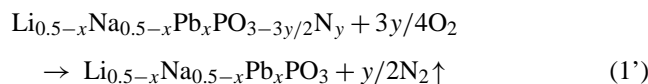
Glass transition temperature ( $T_g$ ), dilatometric softening temperature ( $T_s$ ) and coefficient of thermal expansion (CTE), measured in the  $30\text{--}200^\circ\text{C}$  temperature range obtained from the dilatometric curves of some base and oxynitride glasses

Nominal glass composition	$T_g$ ( $\pm 1^\circ\text{C}$ )	$T_s$ ( $\pm 1^\circ\text{C}$ )	CTE $\times 10^{-6}$ ( $\text{K}^{-1}$ ) $_{30-200^\circ\text{C}}$ ( $\pm 1 \times 10^{-6} \text{ K}^{-1}$ )
$\text{Li}_{0.40}\text{Na}_{0.40}\text{Pb}_{0.10}\text{PO}_3$ (10 mol% PbO)	231	247	23
$\text{Li}_{0.25}\text{Na}_{0.25}\text{Pb}_{0.25}\text{PO}_3$ (25 mol% PbO)	244	264	18
$\text{Li}_{0.10}\text{Na}_{0.10}\text{Pb}_{0.40}\text{PO}_3$ (40 mol% PbO)	278	300	17
$\text{Li}_{0.25}\text{Na}_{0.25}\text{Pb}_{0.25}\text{PO}_{2.82}\text{N}_{0.12}$	273	291	17
$\text{Li}_{0.25}\text{Na}_{0.25}\text{Pb}_{0.25}\text{PO}_{2.64}\text{N}_{0.24}$	286	310	16
$\text{Li}_{0.25}\text{Na}_{0.25}\text{Pb}_{0.25}\text{PO}_{2.40}\text{N}_{0.40}$	310	336	14

$\text{Li}_{0.5-x}\text{Na}_{0.5-x}\text{Pb}_x\text{PO}_{3-3y/2}\text{N}_y$ , a progressive oxidation is represented by the following reaction:



$z = 3y/4$  means that a total transformation into oxide has been reached, according to:



As each nitrogen is replaced by 3/2 oxygens, the oxidation reaction gives rise to a weight gain.

A partial lead reduction could be supposed a priori to occur during ammonolysis because of the strong reducing character of ammonia. However, it is worth mentioning that there was no indication of metallic lead in any of the oxynitride glass samples, as confirmed by X-ray diffraction and scanning electron microscopy. Consequently, the weight gain of the oxynitride glasses is only attributed to a progressive replacement of nitrogen by oxygen.

The DSC and TG graphs in air of the oxynitride glass composition  $\text{Li}_{0.25}\text{Na}_{0.25}\text{Pb}_{0.25}\text{PO}_{2.33}\text{N}_{0.45}$  (25 mol% PbO) for a particle size distribution of 63–100  $\mu\text{m}$  are shown in Fig. 1. The endothermic effect at 311  $^\circ\text{C}$  corresponds to the glass transition temperature. Two exothermic peaks are centered at  $\sim 385$  ( $T_{1-\text{max}}$ ) and  $\sim 467$   $^\circ\text{C}$  ( $T_{2-\text{max}}$ ), each one being associated with a weight gain, thus evidencing two different oxidation steps of the oxynitride glass. Then, at higher temperature ( $>500$   $^\circ\text{C}$ ), the weight starts again to increase.

The total weight gain calculated –and confirmed experimentally – for the transformation of  $\text{Li}_{0.25}\text{Na}_{0.25}\text{Pb}_{0.25}\text{PO}_{2.33}\text{N}_{0.45}$  into  $\text{Li}_{0.25}\text{Na}_{0.25}\text{Pb}_{0.25}\text{PO}_3$  is 3.3%. By comparison, the percentages deduced from Fig. 1 for each oxidation step are 0.34 and 0.36%, respectively, i.e., a total of 0.7% of the initial sample weight, which only corresponds to  $\sim 20\%$  of that assumed for complete oxidation. So, the weight gain

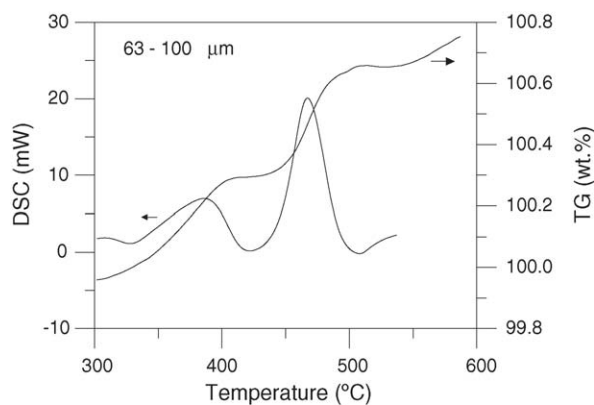


Fig. 1. DSC and TG analyses of the  $\text{Li}_{0.25}\text{Na}_{0.25}\text{Pb}_{0.25}\text{PO}_{2.33}\text{N}_{0.45}$  glass composition with a particle size distribution between 63 and 100  $\mu\text{m}$ .

at higher temperature is related to the major part of oxidation, which proceeds faster in melts with lower viscosities.

However, oxynitride glasses are not adequate for application in this temperature range because of too low viscosity values – and a clear lack of stability – that is why this work is preferentially focused on the oxidation process below 500  $^\circ\text{C}$ .

An important parameter affecting the oxidation is the glass viscosity and its change with temperature. Rheological measurements of the oxide base glass  $\text{Li}_{0.25}\text{Na}_{0.25}\text{Pb}_{0.25}\text{PO}_3$  (25 mol% PbO) have been reported recently by the authors,<sup>30</sup> showing that viscosity decreases rapidly when temperature increases in the 300–500  $^\circ\text{C}$  range ( $\log \eta = 8.48$ , at 300  $^\circ\text{C}$ ;  $\log \eta = 2.01$ , at 475  $^\circ\text{C}$ ). There are no results about the viscosity–temperature relationship of the studied oxynitride glasses, however a quite similar viscosity–temperature dependency may be assumed while considering anyway that viscosity increases as the nitrogen content increases in the glasses. In all cases the sintering taking place during heating, which comes under a viscous flow mechanism, and the consequent change in the specific surface area of the powders are clearly affected by the viscosity–temperature behaviour. At temperatures near 300  $^\circ\text{C}$ , sintering take place still at a very slow rate and the glass particles keep their integrity. Then, the oxidation proceeds over the surface of the glass particles, and the oxidized layer formed limits further progression of the oxidation towards the bulk particles. When the temperature increases the sintering rate of the glass particles also does so. This reduces the specific surface area and gives progressively rise to a melt whose surface is renewed from the inner melt, as a consequence of the decreasing viscosity which favours diffusion, and therefore continuously re-oxidized.

Then, the observed phenomenon can be interpreted as processes involving successively the surface of the glass particles and the surface of the melt, both cases by oxygen diffusion. The second step takes place once the viscosity has decreased enough to allow a faster sintering between the glass particles and, finally, the melting of the glass. So, an important role is played by the viscosity–temperature relationship, as it determines the beginning of the second oxidation step. The very small weight gains observed after the two first oxidation steps cannot be associated with any inhomogeneous character of the nitrated sample nor with a specific behaviour of the two different nitrogen species above mentioned.

This study first reveals a significantly different behaviour towards oxidation of these alkali lead oxynitride phosphate glasses from that is commonly observed in crystalline nitride-type powders for which a regular oxidation takes place from the oxidation threshold.

Fig. 2 depicts two isothermal TG curves obtained with the glass  $\text{Li}_{0.25}\text{Na}_{0.25}\text{Pb}_{0.25}\text{PO}_{2.49}\text{N}_{0.34}$  with particle size 63–100  $\mu\text{m}$  at temperatures chosen a little bit lower than  $T_{1-\text{max}}$  and  $T_{2-\text{max}}$  corresponding to this composition. Both graphs show an asymptotic behaviour as a function of time, with a weight gain higher at 480  $^\circ\text{C}$  than at 350  $^\circ\text{C}$  as expected from thermally activated phenomena. Fig. 3 plots the TG of the isothermal treatment at 480  $^\circ\text{C}$  as a function of  $t^{1/2}$ . A

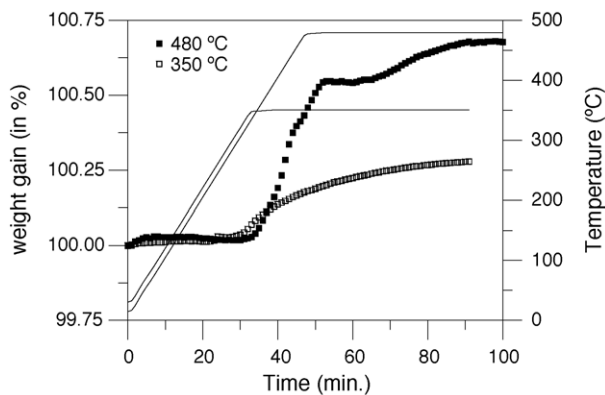


Fig. 2. TG isothermal analyses at 350 and 480 °C for the  $\text{Li}_{0.25}\text{Na}_{0.25}\text{Pb}_{0.25}\text{PO}_{2.49}\text{N}_{0.34}$  glass composition.

linear behaviour is observed, thus confirming that the second oxidation step is a diffusion controlled process.

### 3.1. Influence of an increasing nitrogen content

TG analyses of oxynitride glass samples with N/P atomic ratios equal to 0.24, 0.34 and 0.45, and a particle size distribution between 63 and 100  $\mu\text{m}$ , are represented in Fig. 4. The three curves show a weight increase from  $\sim 300$  °C in a two-step process, with a higher amplitude of the first step as the nitrogen content increases. It has been mentioned above that the viscosity of the oxynitride glasses increases as the nitrogen content increases, as a consequence, in particular, of the higher glass network cross-linking produced by the nitrogen incorporation.<sup>22</sup> So, the higher the temperature corresponding to a given viscosity value, the slower the sintering rate at a given temperature, i.e., the change in the specific surface area. Consequently, the higher nitrogen content the surface oxidation lasts later and the bulk oxidation of the second step

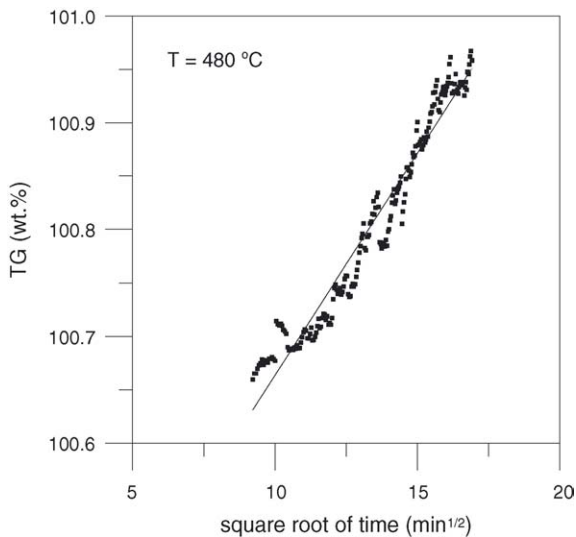


Fig. 3. TG isothermal analysis at 480 °C as a function of the square root of time.

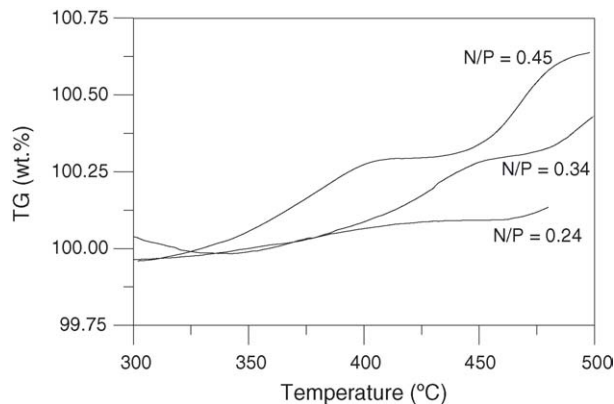


Fig. 4. TG analyses of  $\text{Li}_{0.25}\text{Na}_{0.25}\text{Pb}_{0.25}\text{PO}_{3-3x/2}\text{N}_x$  oxynitride glasses for  $x = 0.24, 0.34$  and  $0.45$ .

also starts later since the sintering of the glass particles will be delayed due to the higher viscosity. Then, it gives rise to a first oxidation step of higher amplitude.

### 3.2. Influence of the base glass composition

Fig. 5 depicts the TG curves of three oxynitride glass samples with the same nitrogen to phosphorous ratio (N/P = 0.45) and different PbO contents, 10, 25 and 40 mol%. The particle size distribution was between 63 and 100  $\mu\text{m}$  for all the three samples.

It appears that the two-step oxidation process closely depends on the PbO content. Whereas the first step begins approximately at  $\sim 300$  °C in all cases, the temperature from which the second step takes place increases when the PbO content increases. As a consequence, the region of constant weight between both steps, which the largest for the 40 mol% PbO glass, is quite difficult to observe for 10 mol% PbO in the conditions studied. Further, Fig. 6 displays the DSC curves of the same three oxynitride compositions. An endothermic effect corresponding to the glass transition temperature, and

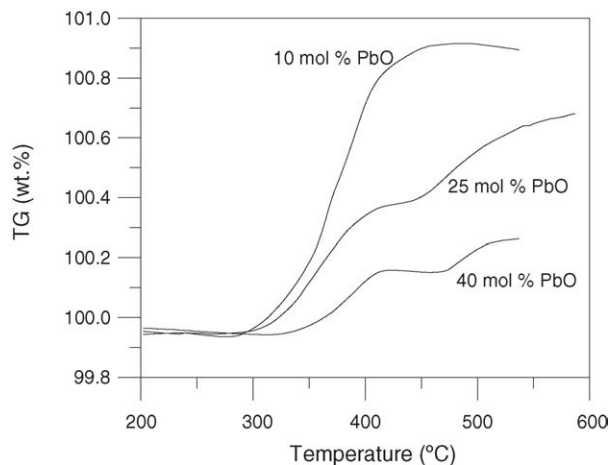


Fig. 5. TG analyses of  $\text{Li}_{0.5-y}\text{Na}_{0.5-y}\text{Pb}_y\text{PO}_{3-3x/2}\text{N}_x$  glasses for  $y = 0.1, 0.25$  and  $0.4$ , and  $x = 0.45$ .

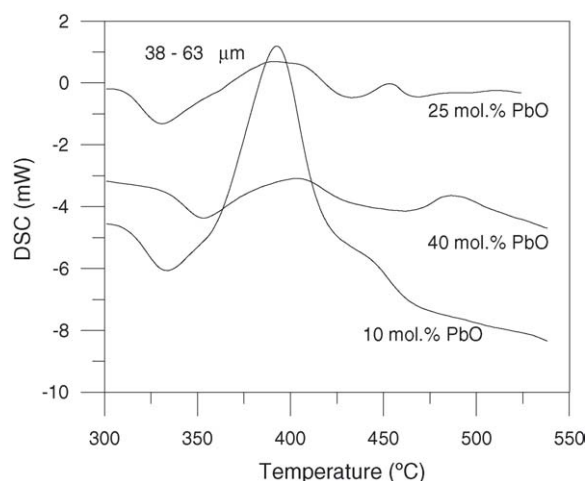


Fig. 6. DSC analyses of  $\text{Li}_{0.5-y}\text{Na}_{0.5-y}\text{Pb}_y\text{PO}_{3-3x/2}\text{N}_x$  glasses for  $y=0.1$ , 0.25 and 0.4, and  $x=0.45$  (particle size 38–63  $\mu\text{m}$ ).

two clear exothermic ones related to the two oxidation steps can be observed in all cases. The 10 mol% PbO glass shows an important exothermic effect at 393 °C, with a small shoulder at 445 °C, whereas the other glasses show two clearly differentiated exothermic effects at 391 and 454 °C (25 mol% PbO), and 404 and 486 °C (40 mol% PbO). So, it is confirmed that both separate oxidation processes take place consecutively whatever the PbO content is, even in the case of the 10 mol% glass where it is not possible to conclude at first sight.

On the other hand, Table 2 gathers the glass transition temperatures of these oxynitride glasses. Whereas the  $T_g$  are very similar for the glasses containing 10 and 25 mol% PbO, the measured  $T_g$  for 40 mol% PbO is 20 °C higher. Such analogous behaviour has already been observed in the variation of the glass transition temperatures of the corresponding  $\text{Li}_{0.5-y}\text{Na}_{0.5-y}\text{Pb}_y\text{PO}_3$  oxide glasses.<sup>31</sup> While low PbO contents induce only a small increase in  $T_g$  a major one takes place between 25 and 50 mol% PbO. When PbO is substituted for alkali oxides, the glass viscosity is expected to raise. According to this, the oxidation temperatures also increase with PbO content, particularly above 25 mol% PbO. This is related to the higher strengthening of the glass network due

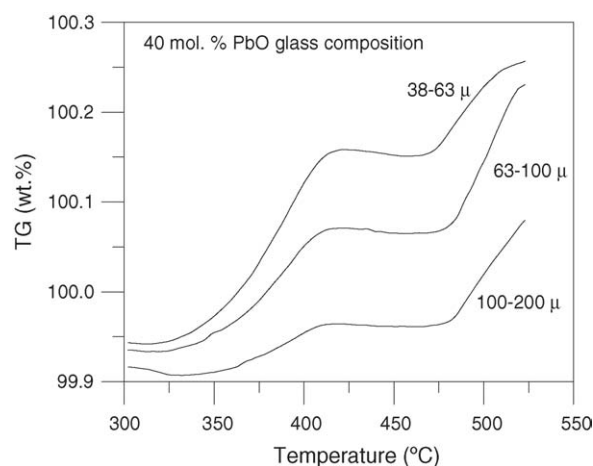


Fig. 7. TG analyses of the  $\text{Li}_{0.1}\text{Na}_{0.1}\text{Pb}_{0.4}\text{PO}_{2.36}\text{N}_{0.43}$  glass composition with particle size distributions of 38–63  $\mu\text{m}$ , 63–100  $\mu\text{m}$  and 100–200  $\mu\text{m}$ .

to the high ionic field strength of  $\text{Pb}^{2+}$  cations, which prevails over those of  $\text{Li}^+$  and  $\text{Na}^+$  at high substitution rate.

Considering that the effect of lead is similar in both oxide and oxynitride glasses we state that its increasingly content affects the oxidation process as follows:

- Lead reduces oxygen diffusion and the weight gain by oxidation is quantitatively lower when PbO content increases as seen in Fig. 5.
- It increases glass viscosity shifting the beginning of both oxidation steps to higher temperatures, as also seen in Fig. 5.
- Lead produces an increase of the glass stiffness, thus reducing the glass fragility by affecting the viscosity–temperature dependency. So, start of the second step may be delayed since the sintering of the glass particles will take place later.

### 3.3. Influence of the particle size distribution

Fig. 7 shows the TG curves obtained for the  $\text{Li}_{0.10}\text{Na}_{0.10}\text{Pb}_{0.40}\text{PO}_{2.36}\text{N}_{0.43}$  composition and different particle size distributions of the glass powders. The weight gain correspond-

Table 2

Glass transition temperatures ( $T_g$ ) obtained from DSC analyses of  $\text{Li}_{0.5-y}\text{Na}_{0.5-y}\text{Pb}_y\text{PO}_{3-3x/2}\text{N}_x$  glasses ( $y=0.1$ , 0.25 and 0.4;  $x=0.45$ )

$y$ in $\text{Li}_{0.5-y}\text{Na}_{0.5-y}\text{Pb}_y\text{PO}_{3-3x/2}\text{N}_x$	Particle size distribution ( $\mu\text{m}$ )	$T_g$ values (°C)	Average value (°C)
0.10	38–63	312.1	312.1
	63–100	312.8	
	100–200	311.3	
0.25	38–63	311.6	311.2
	63–100	311.9	
	100–200	310.2	
0.40	38–63	330.7	332.1
	63–100	333.6	
	100–200	332.0	

ing to the first oxidation step increases logically as the particle size decreases, i.e., as the specific surface area is higher, according to a surface oxidation mechanism. On the other hand, Table 2 shows that the  $T_g$  values are not particle size dependent as expected.

#### 4. Conclusions

This study proves that oxynitride phosphate glasses (illustrated here with alkali lead glasses) are promising sealing materials, as low-melting materials with high thermal expansion coefficients, even if used in an oxygenated atmosphere.

From the recorded thermal curves, the other following conclusions can be given. Oxidation of oxynitride glass powders proceeds, in a first step, through a surface oxidation and, in a second one, by the bulk glass oxidation which is controlled by diffusion. This second step takes place once the viscosity of the glass has decreased enough to allow oxygen diffusion inside the glass and sintering of the glass particles is reached to allow continuous surface renewing.

As the nitrogen content increases, the sintering process of the glass particles becomes slower and the surface oxidation higher. A similar study, as a function of the glass composition, i.e., varying the lead content, confirms that there are two separate processes. For both of them, intensity and starting oxidation temperature are greatly influenced by the stiffness of the glass network through the nature of the modifier cations and, indeed, the viscosity–temperature behaviour along the temperature increasing during oxidation. The glass composition and, therefore, viscosity, determine the oxidation rate. Thus, the faster the decrease in viscosity, the earlier and intense the oxidation.

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