



## Impact of nitridation of metaphosphate glasses on liquid fragility



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### ABSTRACT

Oxynitride glasses are mixed-anion glasses, in which the oxygen atoms have been partially substituted by either two-fold ( $N_d$ ) or three-fold ( $N_t$ ) coordinated nitrogen atoms, introducing additional bonds and thereby constraining the glass network and enhancing the atomic packing density. Phosphate glasses are more prone to undergo nitridation via ammonolysis at relatively low temperature compared to other types of oxide glasses, but here the question is how the nitridation influences the glass transition, structure, and dynamics in phosphate glasses. Here, we answer this question by taking sodium and lithium metaphosphate oxynitride glasses as model systems. Using differential scanning calorimetry (DSC), we measure the effect of the atomic nitrogen/phosphorus (N/P) ratio on the glass transition temperature ( $T_g$ ), jump in isobaric heat capacity at the glass transition ( $\Delta C_p$ ), glass transition width ( $\Delta T_g$ ), and liquid fragility index ( $m$ ) of these model glasses. The results show that the nitridation causes an increase in the atomic packing density and  $T_g$ . In addition,  $\Delta T_g$  increases and  $m$  decreases with increasing N/P, both implying that the liquids become stronger upon nitridation, whereas  $\Delta C_p$  does not vary systematically with N/P within the error range. We discuss the origin of these changes in terms of the underlying changes in the short- and intermediate-range order structures, as detected by Raman spectroscopy.

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## 1. Introduction

Oxynitride glasses exhibit superior properties, e.g., their glass transition temperature, viscosity at comparable temperatures, density, refractive index, electrical conductivity, microhardness, and elastic moduli are higher than the corresponding oxide glasses, and the coefficient of thermal expansion is lower. Oxynitride glasses are typically synthesized by partially replacing two-fold coordinated oxygen atoms with three-fold coordinated nitrogen atoms, and this can be done in a very wide range of oxide glass systems, e.g. phosphate [1], phosphosilicate [2], silicate [3], aluminosilicate [4], and fluoroaluminosilicate glasses [5]. Generally, the physical properties of oxynitride glasses vary linearly with the nitrogen content as compared with the corresponding nitrogen-free parent glass, and the improvement in various optical and physical-chemical properties upon nitridation has given rise to various applications. For example, as LED phosphor matrices [6], transparent high energy dispersive ballistic materials [7], biomaterials [8], and for the continuously demanding electronic purposes [9].

Phosphate glasses find a variety of technological applications, ranging from highly transparent UV light material with tuning emission bands [10], gain media for high power laser applications [11], cathode materials in batteries [12], and low temperature sealant [13]. Nonetheless, phosphate glasses generally suffer from poor chemical durability

against aqueous solutions, limiting their industrial applications. The chemical durability can be improved through nitrogen incorporation within the phosphate anionic network [14]. The nitridation simultaneously increases the resistance to devitrification and the ionic conductivity [15], the later in a non-linear manner up to N/P ~ 0.25 [16], making phosphorus oxynitride glasses suitable as solid-state glass electrolytes. This is a result of the increase in the ratio of the number of non-bridging oxygen (NBO) to that of bridging oxygen (BO) per tetrahedron (NBO/BO) upon nitrogen incorporation [16], and formation of P–N bonds at the expense of the P–O bonds, ultimately leading to a greater connectivity of the anionic sub-network [17]. Currently, LiPON-type glasses are of interest for lithium micro-batteries, exhibiting excellent cyclability performance ( $>5 \times 10^4$  times) at room temperature [18]. The nitridation kinetics in alkali-lead phosphate glasses [19] and the short- and intermediate-range order structures of such phosphorus oxynitride glasses have been investigated [20–27].

While a calorimetric study of the dynamic properties of SiAlON-type oxynitride glasses has been reported [28], the correlations among the glass transition behavior, structure, and dynamics in oxynitride glasses are not well understood. Studying such correlations for oxynitride glasses can contribute to the general understanding of the nature of the glass transition, glass formation, and relaxation behavior [29]. Specifically, the changing rate of dynamic properties such as the relaxation time or viscosity with temperature at the glass transition temperature ( $T_g$ ), i.e., the liquid fragility index  $m$ , is a structural sensitive parameter [30]. Strong liquids exhibit an Arrhenian viscous behavior over the

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entire range of temperatures, while fragile liquids show a non-Arrhenian behavior. Moreover, the glass transition is accompanied by a jump of the isobaric heat capacity ( $\Delta C_p$ ) through the glass transition, the extent of which is generally higher for a fragile liquid than for a strong one within the same glass series. However, it should be mentioned that rigorous comparison of thermodynamic fragility between two different glass-forming liquids should be made in terms of the ratio between the excess liquid entropy over that of the crystal at liquidus temperature ( $T_{liq}$ ),  $S_{ex}(T_{liq})$ , and the excess entropy at  $T_g$ ,  $S_{ex}(T_g)$ . However, this thermodynamic quantity is composition dependent and for multicomponent oxide glasses it is often difficult to determine this ratio. In some cases, the  $\Delta C_p$  is used as an indirect measure of the thermodynamic fragility since it exhibits a parallel relation with  $m$  and an inverse relation with the width of glass transition region [29]. In the present work, we examine if this is case for the oxynitride binary phosphate glass series with varying N content.

In detail, we study the correlations among glass transition behavior, structure, and dynamics in oxynitride binary phosphate glasses at the metaphosphate composition, i.e.,  $50M_2O-50P_2O_5$  (MNa, Li). The nominal stoichiometry is equal to  $MPO_3-(3x/2)N_x$  (where MLi, Na), based on the equivalency of  $2N^{3-}$  for  $3O^{2-}$  atoms substitution. The nitrogen content in phosphorus oxynitride glasses is expressed through the N/P ratio. The simple phosphate network is made up of P-tetrahedra linked through partially covalent bridging oxygens (BO) to form various phosphate anions, with a distinct  $\pi$ -bonded (PO) oxygen, called terminal oxygen (TO), formed due to the pentavalency of phosphorus. Vitreous  $P_2O_5$  has the structure with a three-dimensional network of  $PO_4$  tetrahedra connected through BOs. These bonds break up to form non-bridging oxygens (NBO) upon the addition of modifier oxides. Ideally, the structure of alkali metaphosphates consists only of chains of polymerized  $(PO_3)_n$  anions, formed by  $Q^2$ -links interconnected through ionic bonds between the NBO and the modifier cations [31]. The nitrogen atoms enter the glass network as di-coordinated nitrogen ( $N_d$ ),  $-N=$  by replacing both the BOs and NBOs, and tricoordinated ( $N_t$ ),  $-N<$ , by replacing only the NBOs [17]. That is, the nitridation takes place through the replacements of  $2N_t \leftrightarrow 3BO$  and  $2N_d \leftrightarrow 1BO + 2NBO$  in accordance with composition (O/P ratio) and the charge-neutrality requirements with respect to the modifying cations [32]. It is noteworthy that nitrogen atoms do not bond to modifier cations or become located at the end of a chain site [24] and the oxynitride structure is then formed by a combination of  $PO_{4-y}N_y$  tetrahedra (i.e.,  $PO_4$ ,  $PO_3N$ , and  $PO_2N_2$ ).

We here focus on binary alkali metaphosphate glasses, as they can yield higher nitrogen content compared to phosphate glasses containing multivalent modifier cations [33]. Furthermore, the simpler the system is, the more information one can obtain. In order to determine the dynamic properties of the  $MPO_3-(3x/2)N_x$  phosphorus oxynitride glasses, we perform differential scanning calorimetry (DSC) measurements, during which argon is being used as purge gas to avoid the oxidation of the samples. We explore the impact of the nitrogen content on both  $m$  and  $\Delta C_p$ . The calorimetric results will be correlated with the atomic packing density and network structure as studied by Raman spectroscopy. Our approach will contribute to revealing and understanding the structure-property correlations of this class of glasses. Moreover, by using the phosphorus oxynitride glasses as a model system, our study will enhance the general understanding of glassy dynamics.

## 2. Experimental procedure

### 2.1. Sample preparation

First, sodium and lithium metaphosphate base glasses  $50Na_2O(Li_2O) \cdot 50P_2O_5$  (in mol%) were prepared by using the melt-quenching technique. We used reagent grade raw materials of carbonates and di-ammonium hydrogen phosphate:  $Na_2CO_3$  and  $Li_2CO_3$  (99%, Aldrich) and  $(NH_4)_2HPO_4$  (98% min, Scharlau).

The appropriate amounts of raw materials were ground and mixed to form 75 g of each glass. These batches were first calcined at 400 °C for at least 15 h to release gases and subsequently melted in an electrical furnace for 2 h at 800 °C in porcelain crucibles. The preparation route used for the present study is the same followed for similar alkali phosphate glasses in previous work [34], where chemical analysis by inductively coupled plasma spectroscopy showed no, or minimal, contamination with  $SiO_2$  or  $Al_2O_3$  (less than ~0.25 wt.%).

The analogous oxynitride glasses were obtained by remelting the bulk oxide glasses under ammonia flow (<400 ppm  $H_2O$ ) following the reaction:  $Na/LiPO_3 + xNH_3 \rightarrow Na/LiPO_3-(3x/2)N_x + (3x/2)H_2O$ . This method was chosen, since traditional batch melting using nitride compounds can result in volatilization of some melt constituents, particularly for phosphate melts [2], while melting in  $N_2$  atmosphere is insufficient to promote the melt reaction with molecular nitrogen. The degree of nitrogen incorporation is mainly dictated by the exposure time and temperature of the melt to the flowing ammonia. The reaction rate increases with temperature, but due to partial decomposition of the melt, accompanied by phosphorus losses in the form of phosphine ( $PH_3$ ), the maximum temperature should be <800 °C [35]. We performed the nitridation by adding 2–3 g of base oxide glasses in a graphite crucible and inserting it into a gas-tight mullite horizontal tube furnace. The samples were placed in the furnace at room temperature and then heated under  $N_2$  gas flow. When the furnace reached the pre-determined processing temperature (650–785 °C), the gas flow was switched from  $N_2$  to  $NH_3$  flow (500  $cm^3/min$ ) and the samples were kept under these conditions for 1–7 h. The nitridation temperature and time were varied in order to obtain samples with different N/P ratios. During the cooling of the furnace to room temperature, the gas was switched back from  $NH_3$  to  $N_2$ . After removal from the graphite crucible, the samples were kept in desiccators due to their hygroscopic nature.

The non-crystalline nature of all samples after nitridation was confirmed by X-ray diffraction (XRD) analysis. We determined the nitrogen content of the oxynitride glasses using the inert gas fusion method in a differential  $N_2/O_2$  LECO TC-436 analyzer, performing at least two analyses per sample. The measured concentration of N (in wt.%) is then converted to the N/P ratio, which is the conventional expression for nitrogen content in phosphorus oxynitride glasses, and according to the glass formulation  $MPO_3-(3x/2)N_x$ ,  $x = \text{nitrogen content} = N/P$ . The average standard deviation for  $N_2$  determination is  $\pm 0.3$  wt.%, which corresponds to  $\pm 0.02$  in the N/P ratio. For the Na and Li series, we obtained glasses with N/P ratios between 0–0.50 and 0–0.63, respectively (see Table 1). The M/P ratios in such phosphate glasses have previously been found to be the same before and after ammonolysis [35].

### 2.2. Calorimetric measurements

The DSC measurements were performed using a simultaneous thermal analysis instrument (STA 449 F1 Jupiter, Netzsch). To determine the isobaric heat capacity curves, a baseline measurement was performed initially with two empty Pt/Rh crucibles. A calibration run against a standard material (sapphire) with known heat capacity was conducted afterwards. In order to ensure sufficient thermal contact between the sample and the bottom of the crucible, the samples were flat polished in ethanol and placed in the sample crucible after removing the sapphire. The samples were heated in argon at 10 K/min to a temperature of ~70 K above the estimated glass transition temperature and finally cooled down to room temperature at 10 K/min. Each sample was subjected to two consecutive runs of heating (upscan) and cooling (downscan) at the same rate ( $q_h = q_c = 10$  K/min). This procedure is used to eliminate thermal history effects of the sample during the first scan, i.e., the second upscan (standard scan) records the enthalpy response of a sample with a known thermal history.

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