



## Pressure-induced structural transformations in phosphorus oxynitride glasses



Mouritz N. Svenson<sup>a</sup>, G. Laura Paraschiv<sup>a</sup>, Francisco Muñoz<sup>b</sup>, Yuanzheng Yue<sup>a</sup>, Sylwester J. Rzoska<sup>c</sup>, Michal Bockowski<sup>c</sup>, Lars R. Jensen<sup>d</sup>, Morten M. Smedskjaer<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry and Bioscience, Aalborg University, 9220 Aalborg, Denmark

<sup>b</sup> Ceramics and Glass Institute (CSIC), 28049 Madrid, Spain

<sup>c</sup> Institute of High Pressure Physics, Polish Academy of Sciences, Warsaw 00-142, Poland

<sup>d</sup> Department of Mechanical and Manufacturing Engineering, Aalborg University, 9220 Aalborg, Denmark

### ARTICLE INFO

#### Article history:

Received 24 June 2016

Received in revised form 25 August 2016

Accepted 26 August 2016

Available online xxx

#### Keywords:

Oxynitride glasses

Hot compression

Densification

Structure

Solid state NMR

### ABSTRACT

The structure-property relations of permanently densified sodium metaphosphate oxynitride glasses ( $\text{NaPO}_3 -_{3x/2}\text{N}_x$ ) with varying N/P ratio are investigated. Densification of the bulk samples is achieved through 1 GPa isostatic compression at the glass transition temperature. The pressure-induced structural transformations are characterized by Raman spectroscopy and solid state  $^{31}\text{P}$  and  $^{23}\text{Na}$  NMR spectroscopy, whereas the glass hardness and brittleness are quantified through Vickers indentation. Nitridation of the ambient pressure sodium metaphosphate glass ( $\text{NaPO}_3$ ) results in a step-wise conversion of  $\text{PO}_4$  units into  $\text{PO}_3\text{N}$  and  $\text{PO}_2\text{N}_2$  oxynitride species. Upon hot compression, the glasses become permanently denser and harder, but also more brittle. This pressure-induced densification is not accompanied by changes in the types or fractions of the structural units for the  $\text{NaPO}_3$  glass. In contrast, densification of the oxynitride glasses ( $\text{N/P} > 0$ ) is accompanied by pressure-induced structural transformations between the oxynitride species. Based on the  $^{31}\text{P}$  NMR results, a structural mechanism for these transformations is proposed.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

The mechanical properties of glass are important for a wide range of applications. These properties are governed by chemical composition, forming history, and post-treatment methods. Various post-treatment methods for glass strengthening are currently being applied in industry, e.g., thermal tempering, chemical strengthening, and surface crystallization [1–4]. However, the relatively new approaches, nitridation of oxide glass [5–11] and permanent densification through hot compression [12–16], are not widely applied. These approaches have, however, been found to efficiently modify the structure and mechanical properties of glass, e.g., increase the hardness. Here, we investigate the combined effect of nitridation and hot compression on the structure and mechanical properties of a sodium metaphosphate ( $\text{NaPO}_3$ ) glass system. The sodium metaphosphate composition was chosen due to its ease of nitridation via ammonolysis, as other more thermally stable glass compositions (e.g., silicates) require higher processing temperatures and usually result in less homogenous glasses [17].

Pure phosphate glass ( $\text{P}_2\text{O}_5$ ) has a three-dimensional network structure of  $\text{PO}_4$  tetrahedra connected through covalent bridging oxygens

(BOs) and with a distinct  $\pi$ -bonded ( $\text{P}=\text{O}$ ) oxygen, called terminal oxygen (TO). Upon the addition of modifier oxides, these bonds break up to form non-bridging oxygens (NBO). This can be described using the  $Q^n$  notation, where  $n$  is the number of BO atoms per  $\text{PO}_4$  tetrahedron and pure  $\text{P}_2\text{O}_5$  glass is therefore built up of  $Q^3$  tetrahedra only. The metaphosphate composition consists ideally only of chains of polymerized ( $\text{PO}_3^-$ )<sub>*i*</sub> anions, formed by  $Q^2$ -links interconnected through ionic bonds between the NBOs and the modifier cations [18].

Upon nitridation, nitrogen atoms are incorporated into the anionic network of the oxide glass. This can be achieved by addition of nitrogen-containing raw materials in the melting batch [19], and combined with high pressure synthesis, pure nitride glasses (i.e., not containing oxygen) have also been formed [20,21]. Alternatively, nitridation of oxide glasses can be achieved by treatment of the glass melt in an anhydrous ammonia atmosphere at elevated temperature [22,23]. The structural consequence of nitridation is the formation of a mixed-anion network, where oxygen atoms have been partially substituted by either two-fold ( $\text{N}_d$ ) or three-fold ( $\text{N}_t$ ) coordinated nitrogen atoms [24,25]. The incorporation of nitrogen atoms increases the degree of network cross-linking, resulting in network compaction [26] and increased glass transition temperature and indentation hardness [5–11].

Permanent densification of glass can be achieved by subjecting glasses to sufficiently high pressure, which is conventionally performed

\* Corresponding author.

E-mail address: [mos@bio.aau.dk](mailto:mos@bio.aau.dk) (M.M. Smedskjaer).

at room temperature in diamond anvil cells or piston cylinder devices [27–29]. Using such methods, high pressures (easily >10 GPa) can be achieved, but only relatively small sample specimens (~mm<sup>2</sup>) can be processed. For mechanical testing, larger samples are typically necessary (~cm<sup>2</sup>), and these can be produced by permanent densification at lower pressure (~1 GPa) by application of elevated temperature during compression [30–33]. Various hot-compressed oxide glasses have been investigated [12–14,16], demonstrating changes in, e.g., coordination number of network polyhedral [14], ring size distributions [34], and compaction of modifier environments [14,35] after compression.

Our earlier work on hot-compressed glasses has focused on the influence of network former (e.g., B<sub>2</sub>O<sub>3</sub> vs. SiO<sub>2</sub> [14]) and modifier species (e.g., Na<sub>2</sub>O vs. K<sub>2</sub>O [16]) on network compaction and property changes after compression. Such studies have enhanced the understanding of the cation influence on structure-property relations in compressed glasses, whereas the influence of anion species has not yet been explored. In this study, we therefore investigate the pressure-induced changes in structure, density, and mechanical properties of NaPO<sub>3</sub> – 3x/2N<sub>x</sub> glasses with varying nitrogen content. Structural changes are characterized by solid state <sup>31</sup>P and <sup>23</sup>Na nuclear magnetic resonance (NMR) spectroscopy, along with Raman spectroscopy, whereas the glass hardness and brittleness are quantified through Vickers indentation measurements.

## 2. Materials and methods

### 2.1. Sample preparation

The sodium metaphosphate glass (50Na<sub>2</sub>O·50P<sub>2</sub>O<sub>5</sub> mol%) was produced by conventional melt-quenching technique with the use of reagent grade raw materials of Na<sub>2</sub>CO<sub>3</sub> (99%, Aldrich) and (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (98% min, Scharlau), as described in detail elsewhere [36]. Traditional batch melting using nitride compounds can be complicated by volatilization of melt constituents, especially in the case of phosphate melts. Therefore, nitridation was performed by ammonolysis [22,23]. After quenching, bulk NaPO<sub>3</sub> glass samples were re-melted in a graphite crucible placed in a horizontal tube furnace under an anhydrous ammonia flow. The samples were heated from room temperature under a N<sub>2</sub> gas flow to the processing temperature (650–700 °C), at which the N<sub>2</sub> gas was switched to a NH<sub>3</sub> gas flow. The melts were kept under these conditions for 1 to 4 h. The degree of nitrogen incorporation is governed by the time and temperature the melt is exposed to flowing ammonia. As a result, different nitridation temperatures and times yield samples with varying nitrogen contents. The nitrogen content of oxynitride glasses is conventionally stated by their N/P ratio (ratio of nitrogen to phosphorous in the glass) and samples with N/P equal to 0 (base glass), 0.14, 0.24, and 0.37 were produced, as determined by the inert gas fusion method in a differential N<sub>2</sub>/O<sub>2</sub> LECO TC-436 analyzer. Glass transition temperature (*T<sub>g</sub>*) of the glasses was measured using differential scanning calorimetry at a upscan rate of 10 K/min and *T<sub>g</sub>* was found to increase with increasing N/P (see Table 1), as described elsewhere [36].

**Table 1**  
Glass transition temperatures (*T<sub>g</sub>*) and peak parameters from deconvolution of <sup>31</sup>P MAS NMR spectra for all glasses before and after 1 GPa compression. The uncertainties in the NMR determined site populations do not exceed ± 3%.

Glass	<i>T<sub>g</sub></i> (°C)	PO <sub>4</sub>		PO <sub>3</sub> N		PO <sub>2</sub> N <sub>2</sub>	
		Fraction (%)	δ <sup>31</sup> P (ppm)	Fraction (%)	δ <sup>31</sup> P (ppm)	Fraction (%)	δ <sup>31</sup> P (ppm)
NaPO <sub>3</sub>	289	Q <sup>2</sup> = 96, Q <sup>1</sup> + Q <sup>0</sup> = 4	–19.85 (Q <sup>2</sup> )	–	–	–	–
NaPO <sub>3</sub> (1GPa)	–	Q <sup>2</sup> = 96, Q <sup>1</sup> + Q <sup>0</sup> = 4	–19.92 (Q <sup>2</sup> )	–	–	–	–
NaPO <sub>2.79</sub> N <sub>0.14</sub>	305	75.89	–19.70	21.37	s	2.72	1.15
NaPO <sub>2.79</sub> N <sub>0.14</sub> (1GPa)	–	70.80	–19.73	25.61	–8.67	3.58	1.11
NaPO <sub>2.64</sub> N <sub>0.24</sub>	328	55.95	–19.45	38.53	–8.29	5.51	0.92
NaPO <sub>2.64</sub> N <sub>0.24</sub> (1GPa)	–	53.77	–19.43	39.14	–8.31	7.11	1.05
NaPO <sub>2.45</sub> N <sub>0.37</sub>	346	43.02	–18.90	41.25	–8.18	15.73	0.51
NaPO <sub>2.45</sub> N <sub>0.37</sub> (1GPa)	–	41.36	–19.06	45.97	–8.15	12.67	0.80

After nitridation, one sample (~10 × 10 × 2 mm<sup>3</sup>) of each of the four glass compositions was isostatically compressed at 1 GPa at the respective *T<sub>g</sub>*. We note that *T<sub>g</sub>* can change as a function of pressure, but the changes are expected to be small at 1 GPa [37,38]. Hot compression was performed in a multizone cylindrical furnace placed inside a gas pressure chamber, with nitrogen used as the compression medium. The setup is described in detail elsewhere [13]. The samples were heated at a constant rate of 600 K/h to their ambient pressure *T<sub>g</sub>* and pressure was simultaneously increased to 1 GPa. The samples were kept under these conditions for 30 min followed by cooling at 60 K/min down to room temperature, with subsequent decompression at a rate of 30 MPa/min to ambient pressure. X-ray diffraction analysis of the samples showed no signs of crystallization.

### 2.2. Characterization

The density of the samples was determined before and after compression, using Archimedes' principle with ethanol as the auxiliary liquid. The samples were polished prior to the hardness measurements using a Struers LaboPol-5 instrument with silicon carbide paper, followed by ultrasonic cleansing in ethanol. Indentation was performed on the polished samples using a Duramin 5 (Struers A/S) Vickers microindenter. A minimum of 30 indents were performed on each sample, using a load of 0.49 N and a press time of 10 s. Vickers hardness (*H<sub>V</sub>*) was determined from the size of the indent, whereas the brittleness was quantified by the crack to indent size ratio (*c/a*) following earlier work [39]. Error bars reported in the figures represent the standard deviation of the measurements.

The changes in glass structure upon nitridation and hot compression were investigated using Raman spectroscopy and solid state <sup>31</sup>P and <sup>23</sup>Na magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. We note that NMR analyses were not performed on oxygen and nitrogen nuclei, since these experiments would require enrichment of samples with isotopes suitable for NMR analysis, which was considered to be outside the scope of the present study.

Raman spectroscopy was performed using a Renishaw Invia Raman microscope with a 532 nm excitation source. The Raman spectra were processed using an asymmetric least squares baseline correction and area normalization procedure [40]. <sup>31</sup>P MAS NMR spectroscopy was performed on a Bruker ASX 400 spectrometer operating at 161.96 MHz (9.4 T). The pulse length was 2.5 μs with recycle delay of 60 s. A total number of 128 scans were accumulated with a spinning rate of 10 kHz. Solid (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> was used as secondary reference with a chemical shift of 0.82 ppm with respect to H<sub>3</sub>PO<sub>4</sub> (85%). The <sup>31</sup>P NMR spectra were simulated using Gaussian functions, in accordance with the chemical shift distribution of the amorphous state, with dmfit software [41]. <sup>23</sup>Na MAS NMR was also performed on a Bruker ASK 400 spectrometer at 105.9 MHz. A π/2 pulse length of 2.7 μs, 2 s recycle delay, 1024 scans, and 10 kHz spinning frequency were employed. <sup>23</sup>Na MAS NMR spectra were simulated using the Czjcek model [42] with dmfit software [41]. The main NMR parameters obtained, i.e.,

Download English Version:

<https://daneshyari.com/en/article/1480102>

Download Persian Version:

<https://daneshyari.com/article/1480102>

[Daneshyari.com](https://daneshyari.com)