

# The effect of nitrogen on the structure and thermal properties of beryllium-containing Na-(Li)-Si-O-N glasses

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## Abstract

Two oxynitride glass series with the composition of  $35\text{Na}_2\text{O}-5\text{BeO}-(60-x)\text{SiO}_2-x\text{Si}_3\text{N}_4$  and  $9\text{Li}_2\text{O}-27\text{Na}_2\text{O}-5\text{BeO}-(59-x)\text{SiO}_2-x\text{Si}_3\text{N}_4$ , were prepared. The glasses' topography and structure were studied by Scanning Electron Microscopy and Raman spectroscopy. The composition was analyzed by Inductively Coupled Plasma Optical Emission Spectrometer, SEM-EDS and nitrogen and oxygen elemental analyzer. Na-(Li)-Be-silicate glasses were found to contain up to approximately 3.4 (or 5.2 for EDS measurements) at% of N, respectively. The samples were homogenous in their topography and compositions of their cross-sections.

The presence of three-fold coordinated nitrogen atoms in Na-Be-Si-O-N glasses results in higher degree of polymerization as was observed by Raman spectroscopy. The spectrum of analogous glasses with lithium did not show a significant decrease in  $Q^2$  units but exhibit the presence of  $Q^4$  units which also indicates a polymerization of the network. The incorporation of nitrogen in these glasses leads to the increase of the glass transition temperature and thermal stability.

## 1. Introduction

Adding beryllium to silicate glasses opens a very interesting field of research, considering the unique chemical properties of  $\text{Be}^{2+}$  such as the fact that it has the highest field strength (defined as the charge-to-radius ratio) and the highest

38 electronegativity among all alkaline-earth and alkali ions. As a consequence, beryllium  
39 ions exhibit an electronic polarizability ( $\alpha_{\text{Be}^{2+}} = 0.008 \text{ \AA}^3$ ) which is even lower than that  
40 characteristic of network-forming cations such as  $\text{Si}^{4+}$  ( $\alpha_{\text{Si}^{4+}} = 0.033 \text{ \AA}^3$ ) [1].  $\text{Be}^{2+}$  is  
41 always found to be fourfold coordinated to oxygen in crystalline oxides and to form  
42 regular, charged  $[\text{BeO}_4]^{2-}$  tetrahedra [2]. Similarly to  $\text{Al}_2\text{O}_3$ , that can act as network  
43 modifier when  $\text{Al}^{3+}$  ions are octahedrally coordinated or as network former, as charged  
44  $[\text{AlO}_4]^-$  tetrahedra in the presence of other modifiers [3], the role of BeO in a glass  
45 network is both as intermediate glass former which is apparent from the high  $T_g$  of  
46 beryllium-containing glasses [4], and as a glass-modifier [5] when, for example,  
47 considering the silicate Q-unit distribution as monitored by vibrational spectroscopy [6-  
48 8].

49 So far, only few reports exist on the study of the structure and properties of  
50 beryllium-containing glasses [9-14]. In our previous work on beryllium containing  
51 silicate oxide glasses [5] we have discussed structural variations, as probed by IR and  
52 Raman spectroscopy, for BeO substitution of  $\text{SiO}_2$  in  $35\text{M}_2\text{O}-x\text{BeO}-(65-x)\text{SiO}_2$  glasses.  
53 Based on our previous findings [5], we see that beryllium forms charged  $[\text{BeO}_{4/2}]^{2-}$   
54 tetrahedra in the silicate network. The strong cross-linking capacity of these units is  
55 shown by a significant increase of the glass transition temperature for the glass series  
56  $35\text{M}_2\text{O}-x\text{BeO}-(65-x)\text{SiO}_2$  up to 70 °C for  $\text{M}_2\text{O}=\text{Na}_2\text{O}$ ; and 44 °C for the corresponding  
57 mixed Na-Li-glasses. At the same time, the thermal stability decreases (by 107 °C for  
58 Na-glasses and 155 °C for Na-Li-glasses) as BeO substitutes for  $\text{SiO}_2$  up to 15 mol%  
59 BeO. However, as we showed in ref. [5], vibrational spectroscopy suggests the  
60 formation of Si-O-Be bonds though these bonds appear mostly as of non-bridging  
61 oxygen atoms on silicate tetrahedra.

62 Expanding on our previous work, which focused on the role of  $\text{Be}^{2+}$  ions in glass  
63 formation, fundamental scientific questions remain; for example, when considering the  
64 low viscosity of Be-silicate melts [15] which is in contrast with the high  $T_g$  observed in  
65 the system we studied in ref. [5], thus justifying the ongoing research on this glass  
66 system. In the current work, we focus on the effect of N incorporation on the structure  
67 and thermal properties of Be-containing silicate glasses; this adds data on the lightest  
68 alkaline earth cation to the previous studies published on oxynitride alkaline earth  
69 silicate glasses [16-22]. While such glasses constitute a significant group of oxy-nitride  
70 containing systems [16, 23-27], there is no report yet on the Be-Si-O-N glass system.

71 Thus, choosing the Be-Silicate glasses for nitridation studies will contribute significantly  
72 to our understanding of glass formation and structure, and complement studies on Mg,  
73 Ca, Sr and Ba-containing oxy-nitride silicate glasses.

74 Generally, nitrogen incorporation leads to significant improvements of a number of  
75 glass properties such as an increase in glass transition temperature and glass stability  
76 [28]; a higher electrical conductivity [29-31] and dielectric constant; higher refractive  
77 index; as well as higher elastic modulus and hardness [22, 32]. Most of these changes  
78 are due to the fact that nitrogen chemically bonds to silicon or other network forming  
79 elements in the glass network. Nitrogen when substituting for oxygen forms 2 and/or 3  
80 bonds instead of the two bonds of a bridging oxygen [30, 31], and this leads to a more  
81 covalent and stiffer network. The preparation of oxynitride glasses is much more  
82 complex than for the equivalent non-nitrogen glasses as nitridation processes require  
83 high melting temperatures, a reducing atmosphere to prevent the oxidation of the melt  
84 and crucibles suitable for this process [32]. Moreover, even if these requirements are  
85 fulfilled, nitrogen incorporation into the glass network is not always successful and the  
86 obtained nitrogen content can be lower than the target one.

87 The aim of the present work is to elucidate the effects of nitrogen incorporation on  
88 the structure and the thermal properties of beryllium-silicate glasses containing single  
89 and mixed alkali ions. For this purpose, two different glass series with a composition  
90 close to  $35M_2O-5BeO-(65-x)SiO_2-xSi_3N_4$  were prepared. The first glass series has a  
91 high content of  $Na_2O$  (35 mol%), while in the second series 9 mol% of  $Na_2O$  were  
92 substituted by  $Li_2O$ . The glasses of our previous study [5] were found to contain also a  
93 significant content of Al, which is known to have an analogous effect on the structure  
94 and thermal properties of the alkali silicate network as has BeO [6-8]. Aluminum-free  
95 glasses are compared with Al-containing glasses of the previous study [5], in  
96 consideration of the similar roles of Al and Be as intermediate glass formers. This  
97 aspect of the current study is of key importance as many industrial melts are prepared  
98 in alumina-containing refractory material and  $Al_2O_3$  dissolution will alter the  
99 composition, structure and, consequently, the glass properties as shown before for  
100 various glass systems [33-35]. The preparation, structure and thermal properties of  
101 new beryllium containing oxynitride silicate glasses are reported here for the first time.

102

## 103 2. Experimental

### 104 2.1. Glass preparation

105 Two series of beryllium-silicate oxynitride glasses containing alkali ions were  
106 prepared. The first system of glasses has a composition of  $35\text{Na}_2\text{O}-5\text{BeO}-(60-x)\text{SiO}_2-$   
107  $x\text{Si}_3\text{N}_4$  and the second one of  $9\text{Li}_2\text{O}-27\text{Na}_2\text{O}-5\text{BeO}-(59-x)\text{SiO}_2-x\text{Si}_3\text{N}_4$  in mol%, where  
108  $x$  increases from 1 to 5 mol%. The glasses were prepared from mixtures of  $\text{Si}_3\text{N}_4$   
109 (ChemPur GmbH), BeO (99% Alfa Aesar),  $\text{SiO}_2$  (99.99% ChemPur GmbH),  $\text{Na}_2\text{CO}_3$   
110 (99.9+% ChemPur GmbH) and  $\text{Li}_2\text{CO}_3$  (99.999% ALDRICH). Batches of about 1.3  
111 grams of each composition were placed in niobium crucibles (10 mm diameter).  
112 Synthesis was performed under nitrogen atmosphere. The mixtures were melted at  
113 1400–1650 °C, depending on the composition, using a radio frequency furnace [16].  
114 The melting time was about 1 hour. The melts were cooled by turning off the furnace  
115 at the end of the run (the approximately cooling time to room temperature was 1 h).  
116 During heating, a strong exothermic reaction was observed, and some samples  
117 needed to be re-melted in order to obtain a homogenous material. The temperature at  
118 which a melt formed was found to increase with increasing amount of  $\text{Si}_3\text{N}_4$  [16].

119 Table 1 lists the nominal compositions and the IDs of the synthesized samples. For  
120 comparison, Raman spectra and thermal properties from ref. [5] for the four glasses  
121  $35\text{Na}_2\text{O}-65\text{SiO}_2$ ,  $9\text{Li}_2\text{O}-27\text{Na}_2\text{O}-64\text{SiO}_2$ ,  $35\text{Na}_2\text{O}-5\text{BeO}-60\text{SiO}_2$  and  $9\text{Li}_2\text{O}-27\text{Na}_2\text{O}-$   
122  $5\text{BeO}-59\text{SiO}_2$  (in mol%) were included in this study.

123

### 124 2.2. Glass characterization

#### 125 2.2.1. Chemical analysis

126 The chemical composition (lithium, sodium, beryllium and silicon contents) of the  
127 samples was investigated using an inductively coupled plasma optical emission  
128 spectrometer (ICP-OES, Hitachi High-Technologies Corp., Model SPS3520UV-DD).  
129 Measurements were performed after dissolution of the glass powders in a mixture of 2  
130 ml of  $\text{H}_2\text{O}$ , 0.5 ml of HF acid and 5 ml of  $\text{HNO}_3$  acid heated at 105 °C. All ICP-OES  
131 values are listed in Table 1. The error margins of ICP-OES analysis were +/- 1 % for  
132 all elements. Standard substances for ICP measurements were purchased from Kanto  
133 Chemical Co., Inc.

134 Nitrogen and oxygen contents were determined by inert gas fusion technique using  
135 a nitrogen and oxygen elemental analyzer (LECO Corp., TC-436AR). Nitrogen

136 contents were estimated from the thermal conductivity of the N<sub>2</sub> gas and oxygen  
137 contents from infrared absorption of CO<sub>2</sub> gas after combustion with He gas. The  
138 obtained data for O and N contents has an error exceeding 10 %. In Table 1, the  
139 oxygen content under ICP-OES results was determined from the charge requirements  
140 of the analyzed cations.

141

#### 142 *2.2.2. CSLM observations*

143 The topography of the samples was observed using an Olympus LEXT OLS4000  
144 Confocal Scanning Laser Microscope (CSLM). Color imaging was conducted under  
145 white LED light, and 3D images were obtained using a 405 nm laser and  
146 Photomultiplier Detector. The highest objective lens and laser 3D image magnification  
147 used was 100x, with optical magnification of 2160x. CSLM measurements were  
148 conducted on alcohol-cleaned samples surfaces.

149

#### 150 *2.2.3. SEM with EDS*

151 The topography and composition of the samples were additionally investigated  
152 using a scanning electron microscope (SEM), FEI Company Quanta FEG250 with  
153 Energy Dispersive X-ray Spectrometer (EDAX GENESIS Apex Apollo X60).  
154 Measurements were conducted using a 10 kV beam accelerating voltage with a SE-  
155 ETD detector (secondary electron—Everhart-Thornley detector) working in the high  
156 vacuum mode (pressure 10<sup>-4</sup> Pa). EDS analysis was carried out for three areas for  
157 each sample (for exemplar areas see Fig. 2). It was not possible to detect the light  
158 elements Be and Li with this technique. Therefore, we used the target values for Be  
159 and Li contents and the mean values of EDS results obtained for the other elements,  
160 especially Si and Na, to calculate the approximate compositions of all samples  
161 assuming no significant loss of Li and Be during melting. All EDS values are given with  
162 an accuracy of around ± 5% standard deviation. The results are displayed in Table 1  
163 as EDS analyzed glass compositions. The sensitivity of our SEM-EDS equipment  
164 allows to detect nitrogen only in those samples in which the N content was higher than  
165 3 at%. The other samples contain N level below 3 at% (marked in Table1 as N<sub><3</sub>).

166



167        *2.2.4. Raman spectroscopy*

168        Raman spectra were obtained in the range from 100 to 2000  $\text{cm}^{-1}$  with a resolution  
169        of 2  $\text{cm}^{-1}$  with a dispersive confocal Raman microscope (Renishaw inVia) using the  
170        514.5 and 633 nm laser excitation lines. The sample spot size of the Raman  
171        microscope is about 0.5  $\mu\text{m}$  in diameter. Spectra have been normalized to the intensity  
172        of the high frequency envelop at about 1090  $\text{cm}^{-1}$ , to allow for better comparison. Some  
173        spectra were distorted by underlying fluorescence. Here, baseline subtraction was  
174        employed.

175

176        *2.2.5. DTA analysis*

177        The thermal properties of the glasses were investigated by differential thermal  
178        analysis (DTA). DTA measurements were performed up to 1100  $^{\circ}\text{C}$  on powdered  
179        samples placed in  $\text{Al}_2\text{O}_3$  crucibles, under flowing nitrogen with a NETZSCH STA  
180        409PC instrument and a heating rate of 20  $^{\circ}\text{Cmin}^{-1}$ . The onset of an endothermic drift  
181        found on the DTA curve were taken as representing  $T_g$ . The exothermic processes  
182        observed in all samples are correlated with various crystallization processes. The  
183        thermal properties parameters were estimated with the use of dedicated software. The  
184        precision in the determination of thermal processes depends on the selected  
185        temperature range and varies up to  $\pm 2\%$  of the determined value.

186

187        **3. Results and discussion**

188        *3.1. Chemical composition and topography measurements*

189        Ten beryllium-silicate oxynitride glasses containing either sodium and/or lithium  
190        ions were prepared in radio frequency furnace. Melting under nitrogen atmosphere with  
191        addition of  $\text{Si}_3\text{N}_4$  resulted in dark-grayish, shiny and translucent glass samples. The  
192        samples become less shiny and translucent with an increase in  $\text{Si}_3\text{N}_4$ . This change in  
193        color is expected since oxynitride glasses are normally less transparent than the  
194        equivalent oxide glasses. They usually present a greyish-black color and are only  
195        translucent in thin sections [32].

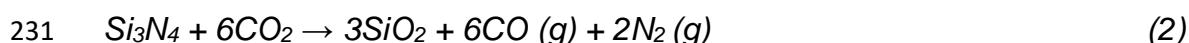
196        The target and analyzed compositions of the (Li)-Na-Be-Si-O-(N) glass series are  
197        listed in Table 1. Samples IDs are based on the nominal  $x\text{Si}_3\text{N}_4$  quantity in mol% ( $x =$   
198        1, 2, 3, 4 or 5) and suggest glass series with sodium ( $x\text{NNaBe}$ ) or sodium and lithium

199 (xNLiNaBe). The compositions were evaluated with three techniques. The nitrogen  
200 content was estimated with the nitrogen analyzer, which is more sensitive for nitrogen  
201 detection than the EDS technique. However, as mentioned earlier, the N results should  
202 be taken as approximate values only, since we could not get all samples measured  
203 with the necessary extraction time for high accuracy. However, N-analysis by gas  
204 analyzer was able to measure low nitrogen levels that increase from 0.9 for glasses  
205 doped with 1 mol% of Si<sub>3</sub>N<sub>4</sub>) to ~3.4 at% for glasses doped with 5 mol% of Si<sub>3</sub>N<sub>4</sub>.  
206 ICP-OES was employed in order to directly measure the light elements lithium and  
207 beryllium which are not detectable by SEM-EDS. All cations (Na, Li, Be and Si) were  
208 found in the glasses in similar levels as expected from the target compositions.

209 SEM-EDS was initially used to confirm the elemental analysis, including Al-  
210 impurities from the crucible. Since the elements Li and Be are too light to be detected  
211 by SEM-EDS, their levels were assumed to equal the nominal compositions and the  
212 presented data added Li and Be levels relative to the analyzed Si content. It is worth  
213 to note that only three samples with lithium addition (3NLiNaBe, 4NLiNaBe and  
214 5NLiNaBe) contain a nitrogen level that could be detected by SEM-EDS (> 3 at%).

215 Overall, the analyzed compositions contain slightly less Si than the target glasses.  
216 The difference is especially obvious for glasses with detectable N content (glasses  
217 3NLiNaBe, 4NLiNaBe and 5NLiNaBe). One explanation could be the formation of the  
218 reduced volatile SiO species during the melting process. For most of glasses, the N  
219 content estimated by SEM-EDS and nitrogen analyzer (ICP-OES in Table 1) are in  
220 good agreement, although the N contents estimated by EDS measurements in three  
221 samples, 3NLiNaBe, 4NLiNaBe and 5NLiNaBe, are slightly higher than those by the  
222 nitrogen analyzer. Since SEM-EDS measurements were done only for three selected  
223 areas, and contents of Li and Be elements could not be determined at all, we decided  
224 to base our discussion on ICP-OES and nitrogen analyzer results.

225 The fact that the estimated N content is generally lower than the nominal (aimed)  
226 N content can be explained by the presence of CO<sub>2</sub> (carbonate) in the raw materials,  
227 which during release acts against N incorporation into the glass network [24]. This is  
228 due to CO<sub>2</sub> from carbonates which may oxidize Si<sub>3</sub>N<sub>4</sub> according to the reactions:



232



233 leading to N<sub>2</sub> loss. Also, Si<sub>3</sub>N<sub>4</sub> can decompose in batch according to:

234



236

237 leading to frothing in O–N glass melt [24]. In this case, N incorporation into the glass  
 238 structure is depressed. Moreover, the vapor pressure of decomposition for Si<sub>3</sub>N<sub>4</sub>  
 239 releasing N<sub>2</sub> can rise above atmospheric pressure at temperatures as low as 1400°C  
 240 [36, 37].

241

242 **Table 1** Glasses IDs, target and analyzed EDS and ICP-OES compositions in at%. For comparison,  
 243 data are included for glasses 35M<sub>2</sub>O–65SiO<sub>2</sub> and 5BeO–35M<sub>2</sub>O–60SiO<sub>2</sub> taken from ref.[5].

Sample ID	Target composition (in at%)	SEM-EDS (in at%)	ICP-OES (in at%)
<b>35Na<sub>2</sub>O–5BeO–(60-x)SiO<sub>2</sub>–xSi<sub>3</sub>N<sub>4</sub></b>			
1NNaBe	Na <sub>24.4</sub> Be <sub>1.7</sub> Si <sub>20.2</sub> O <sub>52.3</sub> N <sub>1.4</sub>	Na <sub>22.3</sub> Be <sub>1.7</sub> Si <sub>21.0</sub> O <sub>54.9</sub> N <sub>&lt;3</sub>	Na <sub>23.6</sub> Be <sub>1.8</sub> Si <sub>21.4</sub> O <sub>52.3</sub> N <sub>0.9</sub>
2NNaBe	Na <sub>23.1</sub> Be <sub>1.7</sub> Si <sub>21.1</sub> O <sub>51.5</sub> N <sub>2.6</sub>	Na <sub>26.8</sub> Be <sub>1.5</sub> Si <sub>18.9</sub> O <sub>52.8</sub> N <sub>&lt;3</sub>	Na <sub>23.2</sub> Be <sub>1.8</sub> Si <sub>22.0</sub> O <sub>51.5</sub> N <sub>1.4</sub>
3NNaBe	Na <sub>22.8</sub> Be <sub>1.6</sub> Si <sub>21.5</sub> O <sub>50.2</sub> N <sub>3.9</sub>	Na <sub>26.2</sub> Be <sub>1.5</sub> Si <sub>19.3</sub> O <sub>53.1</sub> N <sub>&lt;3</sub>	Na <sub>23.1</sub> Be <sub>1.7</sub> Si <sub>22.8</sub> O <sub>50.2</sub> N <sub>2.1</sub>
4NNaBe	Na <sub>22.5</sub> Be <sub>1.6</sub> Si <sub>21.9</sub> O <sub>48.9</sub> N <sub>5.1</sub>	Na <sub>24</sub> Be <sub>1.5</sub> Si <sub>20.3</sub> O <sub>54.2</sub> N <sub>&lt;3</sub>	Na <sub>23.5</sub> Be <sub>1.8</sub> Si <sub>22.8</sub> O <sub>48.9</sub> N <sub>3</sub>
5NNaBe	Na <sub>22.2</sub> Be <sub>1.6</sub> Si <sub>22.2</sub> O <sub>47.6</sub> N <sub>6.3</sub>	Na <sub>22.2</sub> Be <sub>1.5</sub> Si <sub>21.2</sub> O <sub>55</sub> N <sub>&lt;3</sub>	Na <sub>23.8</sub> Be <sub>1.8</sub> Si <sub>23.6</sub> O <sub>47.6</sub> N <sub>3.2</sub>
<b>9Li<sub>2</sub>O–27Na<sub>2</sub>O–5BeO–(59-x)SiO<sub>2</sub>–xSi<sub>3</sub>N<sub>4</sub></b>			
1NLiNaBe	Li <sub>6</sub> Na <sub>18.7</sub> Be <sub>1.7</sub> Si <sub>20.4</sub> O <sub>52.5</sub> N <sub>1.3</sub>	Li <sub>5.8</sub> Na <sub>19.2</sub> Be <sub>1.8</sub> Si <sub>19.7</sub> O <sub>53.6</sub> N <sub>&lt;3</sub>	Li <sub>6.8</sub> Na <sub>16.8</sub> Be <sub>1.8</sub> Si <sub>21.2</sub> O <sub>52.5</sub> N <sub>0.9</sub>
2NLiNaBe	Li <sub>5.9</sub> Na <sub>17.8</sub> Be <sub>1.7</sub> Si <sub>20.8</sub> O <sub>51.2</sub> N <sub>2.6</sub>	Li <sub>5.5</sub> Na <sub>20.5</sub> Be <sub>1.5</sub> Si <sub>19.3</sub> O <sub>53.1</sub> N <sub>&lt;3</sub>	Li <sub>6.9</sub> Na <sub>16.9</sub> Be <sub>1.8</sub> Si <sub>21.6</sub> O <sub>51.2</sub> N <sub>1.5</sub>
3NLiNaBe	Li <sub>5.9</sub> Na <sub>17.6</sub> Be <sub>1.6</sub> Si <sub>21.2</sub> O <sub>49.8</sub> N <sub>3.9</sub>	Li <sub>5.2</sub> Na <sub>19.9</sub> Be <sub>1.4</sub> Si <sub>18.6</sub> O <sub>53.1</sub> N <sub>3.6</sub>	Li <sub>6.9</sub> Na <sub>17.5</sub> Be <sub>1.8</sub> Si <sub>21.8</sub> O <sub>49.8</sub> N <sub>2</sub>
4NLiNaBe	Li <sub>5.8</sub> Na <sub>17.4</sub> Be <sub>1.6</sub> Si <sub>21.5</sub> O <sub>48.6</sub> N <sub>5.1</sub>	Li <sub>4.7</sub> Na <sub>21.8</sub> Be <sub>1.3</sub> Si <sub>17.5</sub> O <sub>49.5</sub> N <sub>5.2</sub>	Li <sub>7</sub> Na <sub>17.6</sub> Be <sub>1.8</sub> Si <sub>22.1</sub> O <sub>48.6</sub> N <sub>2.9</sub>
5NLiNaBe	Li <sub>5.7</sub> Na <sub>17.1</sub> Be <sub>1.6</sub> Si <sub>21.9</sub> O <sub>47.3</sub> N <sub>6.3</sub>	Li <sub>4.8</sub> Na <sub>19.6</sub> Be <sub>1.3</sub> Si <sub>18.6</sub> O <sub>50.7</sub> N <sub>5</sub>	Li <sub>7.1</sub> Na <sub>17.9</sub> Be <sub>1.9</sub> Si <sub>22.5</sub> O <sub>47.3</sub> N <sub>3.4</sub>
<b>35M<sub>2</sub>O–65SiO<sub>2</sub> and 35M<sub>2</sub>O–5BeO–60SiO<sub>2</sub> [5]</b>			
0Na	Na <sub>23.3</sub> Si <sub>21.7</sub> O <sub>55</sub>	Na <sub>19.2</sub> Al <sub>0.5</sub> Si <sub>23.3</sub> O <sub>57</sub>	Na <sub>22.4</sub> Si <sub>21.1</sub> Al <sub>0.5</sub> O <sub>56</sub>
0NaBe	Na <sub>23.7</sub> Be <sub>1.7</sub> Si <sub>20.3</sub> O <sub>54.2</sub>	Na <sub>15.5</sub> Be <sub>1.9</sub> Al <sub>1.1</sub> Si <sub>23.3</sub> O <sub>58.1</sub>	Be <sub>1.8</sub> Na <sub>20.7</sub> Si <sub>20.6</sub> Al <sub>0.8</sub> O <sub>56.2</sub>
0LiNa	Li <sub>6</sub> Na <sub>18</sub> Si <sub>21.3</sub> O <sub>54.7</sub>	Li <sub>5.8</sub> Na <sub>18.4</sub> Al <sub>0.5</sub> Si <sub>20.8</sub> O <sub>54.5</sub>	Li <sub>6.7</sub> Na <sub>17</sub> Si <sub>21.3</sub> Al <sub>0.4</sub> O <sub>54.6</sub>
0NaBeLi	Li <sub>6.1</sub> Na <sub>18.3</sub> Be <sub>1.7</sub> Si <sub>20</sub> O <sub>53.9</sub>	Li <sub>6</sub> Na <sub>14.7</sub> Be <sub>1.8</sub> Al <sub>2.5</sub> Si <sub>19.8</sub> O <sub>55.3</sub>	Li <sub>8</sub> Na <sub>16.6</sub> Be <sub>1.7</sub> Si <sub>17</sub> Al <sub>2.8</sub> O <sub>53.9</sub>

244

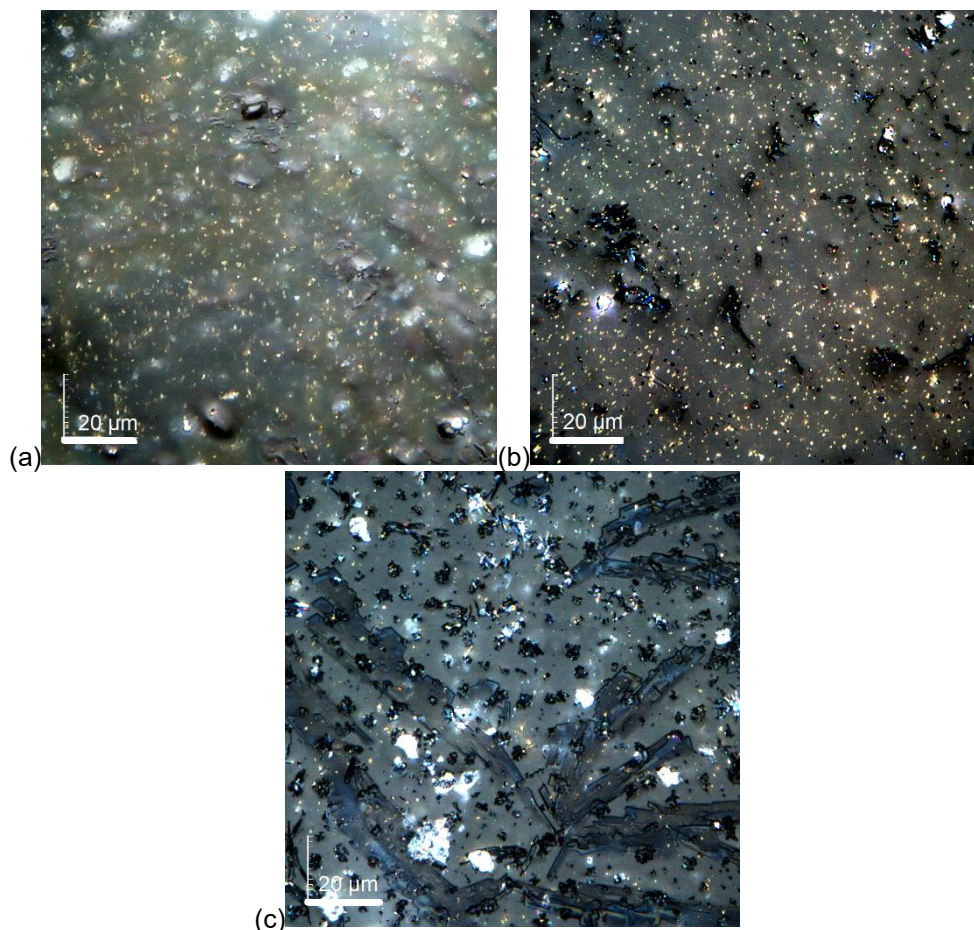
245 Figure 1(a) presents the CSLM image for glass 4NNaBe. Its topography looks  
 246 like a typical glass surface [38]. The other glasses of the xNNaBe series show a similar  
 247 glossy topography with grayish color. The topography of glass 1NLiNaBe is shown in  
 248 Fig. 1(b). Contrary to the samples of the xNNaBe series, it has a less smooth surface  
 249 and contains inhomogeneities. The most significant change is observed for the  
 250 topography of glasses 4NLiNaBe and 5NLiNaBe (Fig. 1(c)). The color of their surfaces  
 251 is darker, and their topography contains even more inhomogeneities.

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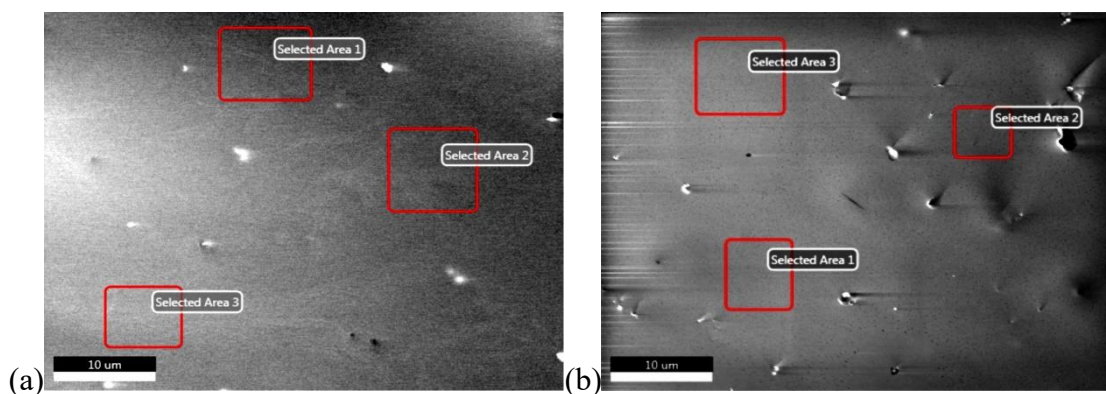


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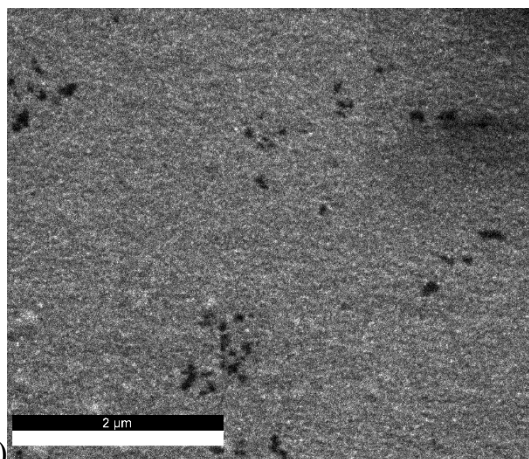
**Figure 1** CSLM micrographs of glasses surfaces: (a) 4NNaBe, (b) 1NLiNaBe and (c) 5NLiNaBe.

259 SEM micrographs of fresh cross-sections of the glasses 3NNaBe and 4NLiNaBe  
260 are presented in Fig. 2 (a) and (b), respectively. Additionally, Fig. 2 (c) depicts the  
261 topography of glass 1NNaBe using a higher magnification. The topography of the  
262 presented samples is characteristic for homogenous glasses, without any evidence for  
263 phase separation or precipitates. Similar micrographs were obtained for all other  
264 glasses discussed in this study.

265



266



267  
268 **Figure 2** SEM micrographs for fractured glasses: (a) 3NNaBe, (b) 4NLiNaBe and (c) 1NNaBe (with  
269 higher magnification).  
270

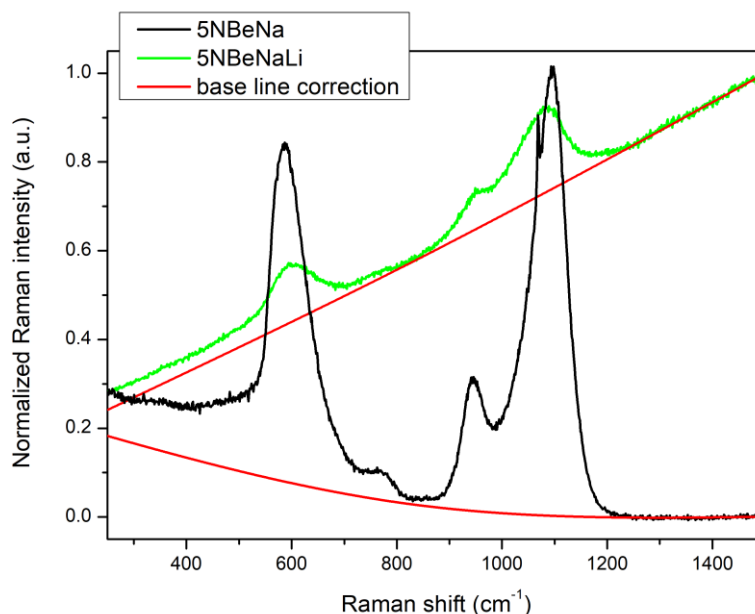
271 *3.2. Vibrational spectroscopy*

272 *3.2.1. Raman spectra of glasses*

273 Raman spectra of representative samples are shown in Figs 3 and 4. For better  
274 understanding of the Raman results we include spectra from reference [5] for the N-  
275 free and Be-free glasses  $65\text{SiO}_2\text{-}35\text{Na}_2\text{O}$  and  $64\text{SiO}_2\text{-}27\text{Na}_2\text{O-}9\text{Li}_2\text{O}$  denoted as 0Na  
276 and 0LiNa in the following discussion, as well as for the N-free beryllate glasses  $5\text{BeO-}$   
277  $60\text{SiO}_2\text{-}35\text{Na}_2\text{O}$  and  $5\text{BeO-}59\text{SiO}_2\text{-}27\text{Na}_2\text{O-}9\text{Li}_2\text{O}$  denoted as 0NaBe and 0NaBeLi. It  
278 should be noted that the last two samples contain traces of Al from dissolution of the  
279 crucible material (see Table 1), while Al inclusion is absent from N-containing glasses  
280 prepared in Nb crucibles.

281

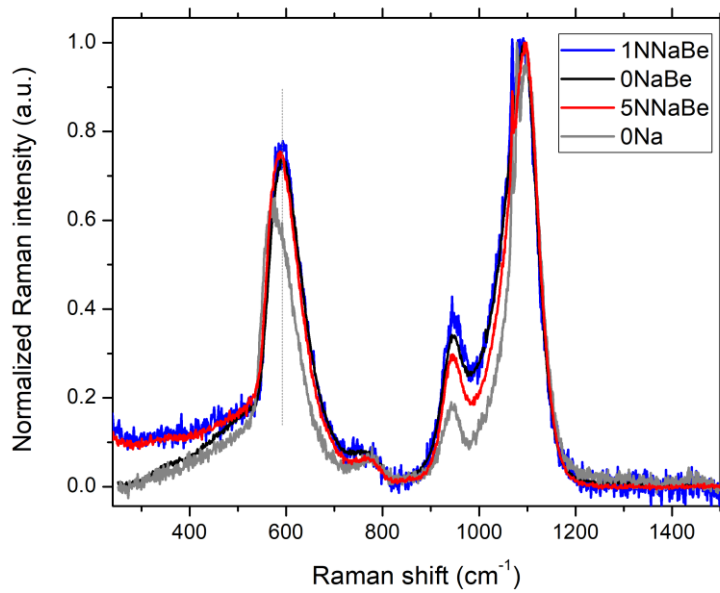
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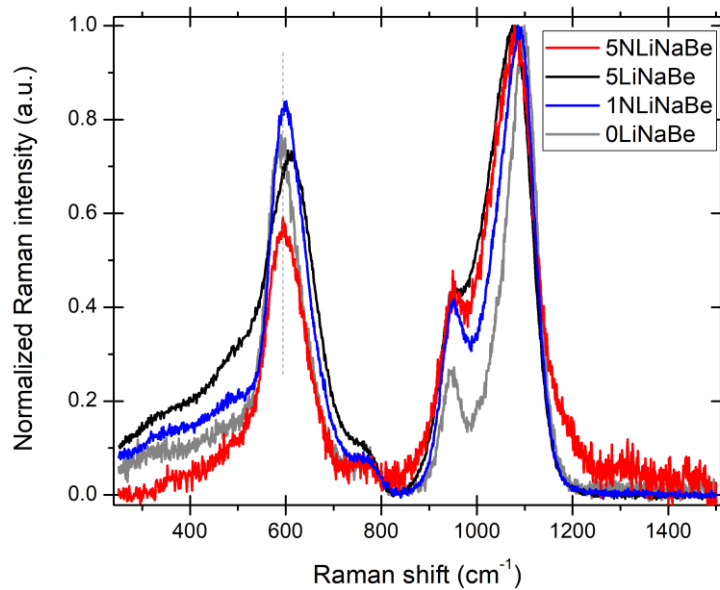
283  
 284 **Figure 3** Raman spectra for exemplar glasses 5NNaBe and 5NLiNaBe, measured using the 633 and  
 285 514.5 nm laser excitation lines, respectively. These spectra are not baseline corrected, but adjusted in  
 286 their intensities for better comparison (red lines give examples for base line subtraction to account for  
 287 the broad fluorescence bands).

288  
 289 As seen in Figure 3, significant fluorescence background was found in the Raman  
 290 spectra of the xN(Li)NaBe series after nitridation. Therefore, background correction  
 291 needed to be conducted for the baseline above 350  $\text{cm}^{-1}$ , and the baseline corrected  
 292 spectra are shown in Figure 4. We note that some spectra exhibited less fluorescence  
 293 with 633 nm instead of 514.5 nm excitation. The use of the 488 nm excitation line  
 294 available to us gave similar fluorescence as the 514.5 nm line. Another option available  
 295 to us was the 785 nm line, but in silicates this line often gives strong artefacts arising  
 296 from Nd impurities which results in a strong fluorescing signal [39].

297



(a)



(b)

298

299

300 **Figure 4** Raman spectra of glasses in the series **(a)** xNNaBe and **(b)** xNLiNaBe (for glass compositions  
 301 see Table 1), measured using the 633 and 514.5 nm laser excitation lines, respectively. For comparison,  
 302 are included the Raman spectra for glasses 35Na<sub>2</sub>O-65SiO<sub>2</sub> (0Na) and 35M<sub>2</sub>O-5BeO-60SiO<sub>2</sub> (0NaBe  
 303 and 0LiNaBe) of ref.[5]. All spectra are baseline corrected and normalized to the intensity of the high  
 304 frequency envelop at about 1090 cm<sup>-1</sup>.

305

306 Exemplar Raman spectra taken from fresh cross-sections of glasses 1N(Li)NaBe  
 307 and 5N(Li)NaBe are presented in Fig. 4a and b, respectively, for glasses from the

308 xNNaBe and xNLiNaBe glass series. The plots also include the Raman spectra of the  
309 N-free glasses 0(Li)Na and 0(Li)NaBe. The spectra of the nitrogen containing glasses  
310 2N(Li)NaBe to 4N(Li)NaBe overlay pretty much the spectra of glasses 1N(Li)NaBe,  
311 especially when considering the uncertainties of fluorescence and base line correction  
312 and are therefore not included in Fig.4.

313 All Raman spectra show a very strong band at  $\sim 1090\text{ cm}^{-1}$ , which is typical for a  
314 high connected silicate network as this band is due to the symmetric stretching mode  
315 of Si-O bonds in  $Q^3$  units,  $\nu(\text{Si-O}) Q^3$  [3, 40-42]. In addition, all spectra show a  
316 pronounced contribution on the low-energy side of the  $1090\text{ cm}^{-1}$  band, reflecting the  
317 presence of  $Q^2$  groups (ca.  $950\text{ cm}^{-1}$ ). The weak Raman feature at  $\sim 770\text{ cm}^{-1}$  is  
318 assigned to the symmetric bending vibration of Si-O-Si bridges, while the intense  
319 Raman band at  $\sim 590\text{ cm}^{-1}$  reflects a combination of stretching and bending modes of  
320 the Si-O-Si bridges [3, 40-42]. This last band depends strongly on the connectivity of  
321 the silicate network, and for a glass structure dominated by  $Q^3$  tetrahedra its position  
322 is observed close to  $570\text{ cm}^{-1}$  [40, 41].

323 For both the Raman spectra of the studied series in Fig.4a and 4b, with and without  
324 lithium addition, we observe the highest  $Q^3$  and lowest  $Q^2$  relative intensities for the  
325 alkali-silicate glasses without beryllium or nitrogen additions (0Na and 0LiNa). As  
326 discussed in detail in our previous work [5], BeO and  $\text{Al}_2\text{O}_3$  substitution for  $\text{SiO}_2$  (as in  
327 0NaBe(Li)), will increase the signature of  $Q^2$  bands as Be-O-Si and Al-O-Si bridges  
328 form between  $\text{SiO}_{4/2}$  and  $[\text{BeO}_{4/2}]^{2-}$  or  $[\text{AlO}_{4/2}]^-$  tetrahedra; both of the latter are charge  
329 balanced by  $\text{Na}^+$  and/or  $\text{Li}^+$  ions from modifier oxides that are in turn not available for  
330 the depolymerization of the silicate network.

331 In the sodium series, the sodium levels are slightly higher in the nitride-containing  
332 xNLiNaBe glasses than the N-free samples, while the silicate content is slightly lower  
333 and the BeO level is lower than the BeO and  $\text{Al}_2\text{O}_3$  levels in the glass 0NaBe. Contrary  
334 to a higher alkali content, which would increase the  $Q^2$  fraction, a lower BeO (and  
335  $\text{Al}_2\text{O}_3$ ) level will decrease the  $Q^2$  content and increase the  $Q^3$  fraction. Compared to  
336 the 0NaBeLi glass, the composition of the nitrated xNLiNaBe glasses is higher in the  
337 silicate content and slightly lower in  $\text{Li}_2\text{O}$  content, while the content of BeO is lower  
338 than the BeO and  $\text{Al}_2\text{O}_3$  level in the glass 0NaBeLi. Therefore, similar changes for  
339 Raman spectra should be observed as for glasses without lithium. From Figure 4, it is  
340 apparent that both effects are of similar magnitude.

341

342

### 343 *3.2.2. Effect of nitrogen addition on Raman spectra*

344 In both the  $x\text{N(Li)NaBe}$  series, the Raman spectrum of the glass with  $x=5$  shows a  
345 higher  $Q^3:Q^2$  ratio than for  $x=1$ , though glasses with  $x=2$  to 4 are closer to  $x=1$  in  
346 appearance. No steady evolution is seen with nitrogen addition, even when comparing  
347 the spectra of the three glasses 3-5N(Li)NaBe for which a significant nitrogen content  
348 could be confirmed by SEM-EDS. The decrease in the  $Q^2$  band for sample 5N(Li)NaBe is  
349 indicative for a higher network polymerization caused by the presence of three-fold  
350 coordinated nitrogen atoms in silicate glasses. Of interest is the spectrum of glass  
351 5N(Li)NaBe (Fig. 4b) which, even though it does not show a significant decrease in  $Q^2$   
352 units, shows a shoulder at about  $1190\text{ cm}^{-1}$  which is indicative of  $Q^4$  units. This feature  
353 signals the polymerization of the network for the sample with the highest nitrogen  
354 addition. The band position of the mixed symmetric stretching-bending modes of Si-O-  
355 Si at about  $590\text{ cm}^{-1}$  is slightly higher for glasses 0(Li)NaBe and 1N(Li)NaBe which are  
356 both more depolymerized, than glasses 0(Li)Na and 5N(Li)NaBe. As discussed before,  
357 the type of polymerization in glasses 0(Li)Na and 5N(Li)NaBe is quite different. Glasses  
358 0(Li)Na have more Si-O-Si bridges, glass 5N(Li)NaBe more Si-N-Si bridges and Si-O-  
359 Be bridges, the oxygen of the latter appearing as non-bridging in the Raman spectra  
360 ( $Q^2$ ,  $Q^3$  units). It should be noted here that  $\text{Si}_3\text{N}_4$  addition will increase the degree of  
361 network polymerization regardless of subsequent  $\text{N} \leftrightarrow \text{O}$  exchange, as more network  
362 former elements (Si) are added to a constant reservoir of network modifiers.

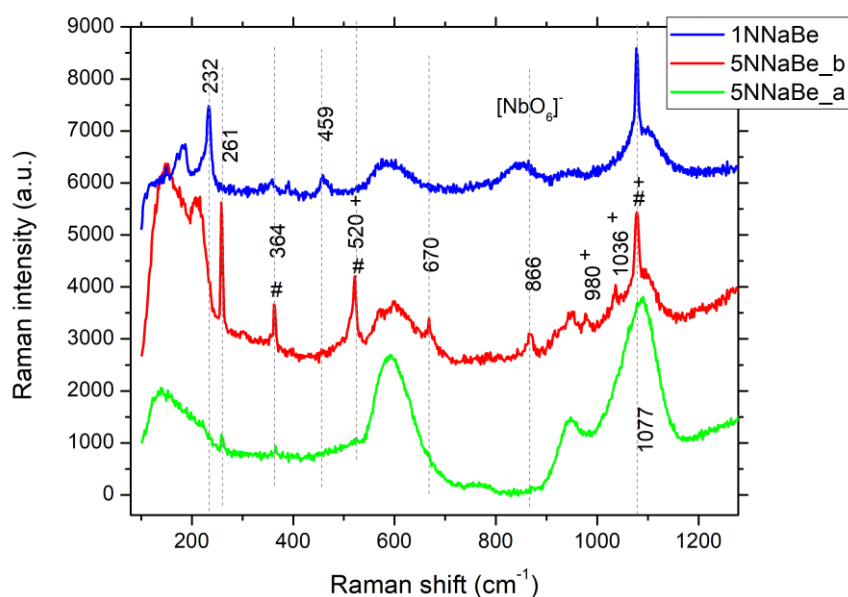
363

### 364 *3.2.3. Raman spectra of the small fraction heterogeneities*

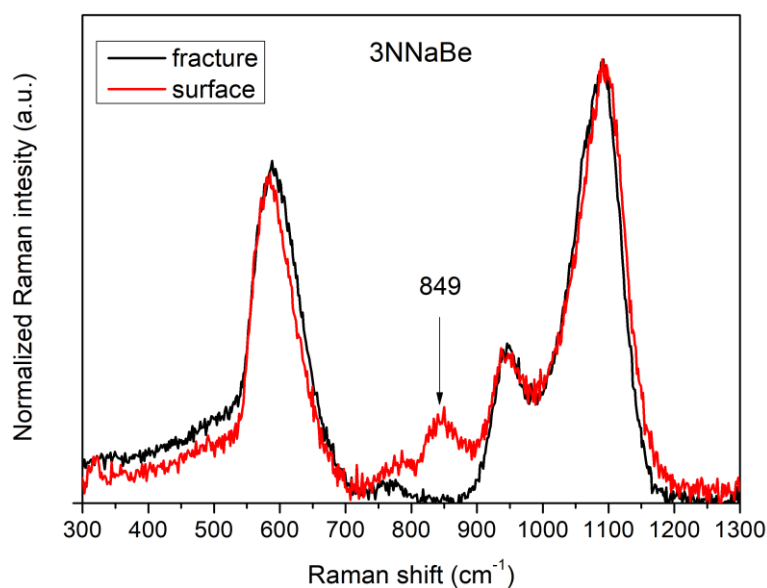
365 While measuring the spectra of N-containing glasses, by focusing the Raman  
366 microscope on vitreous areas of the samples, we noticed the presence of some  
367 crystalline inclusions and impurities from the niobium crucibles. As an example, Figure  
368 5a shows the Raman spectra of such heterogeneous sample spots, where several  
369 spectra show sharp bands at  $1077\text{ cm}^{-1}$  and  $520\text{ cm}^{-1}$ . These bands can be attributed  
370 to crystalline silicates such as  $\text{Na}_2\text{Si}_2\text{O}_5$  [43] or  $\text{Na}_6\text{Si}_8\text{O}_{19}$  [44], while a sharp signal at  
371  $540\text{ cm}^{-1}$  in  $x\text{N(Li)NaBe}$  glasses (not shown in Fig.5a) indicates the formation of  
372 crystalline  $\text{Li}_2\text{Si}_2\text{O}_5$  [45].

373





374 (a)



375 (b)

376 **Figure 5** (a) Raman spectra of heterogeneous spots for glasses 1NNaBe and 5NNaBe and (b)  
 377 Raman spectra of glass 3NNaBe measured on a fresh cross-section (black) and the surface (red)  
 378 which was in contact with the Nb crucible. Sharp bands in (a) marked with # and + indicate the  
 379 formation of crystalline  $\text{Na}_6\text{Si}_8\text{O}_{19}$  ( $Q^3:Q^4=3:1$ ) and  $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ , respectively. Spectra were measured  
 380 using the 633 nm laser excitation line.

381  
 382 The comparison of Raman measurements conducted on the cross-section and  
 383 surface of glass 3NNaBe is displayed in Fig. 5b. The Raman spectrum of the glass

384 surface exhibits an additional band at  $\sim 849\text{ cm}^{-1}$  which can be assigned to highly  
 385 distorted  $\text{NbO}_6$  octahedra [45]. The high polarizability of Nb ions compared to the  
 386 polarizability of silicate cations, results in an exceptional high scattering cross section  
 387 for Nb-O related bands and, thus, traces of dissolved Nb-impurities can be identified  
 388 by Raman spectroscopy. It is of interest to note that we could reproducibly identify Nb-  
 389 related bands when measuring on the original sample surface which was in contact  
 390 with the Nb-crucible. However, the Nb-signature band at  $849\text{ cm}^{-1}$  is absent from the  
 391 spectra taken from within the bulk of glasses by focusing on the inside of broken off  
 392 glass pieces. Thus, the presence of Nb in the glass surface in contact with the crucible  
 393 is a consequence of the synthesis route employed. Contrary to a previous report on  
 394 phosphate glasses [28], no significant amounts of Nb dissolve in the Be-silicate glass  
 395 melt.

396

### 397 3.3. Thermal properties

398 The thermal properties of all  $x\text{NNaBe(Li)}$  glasses were determined from DTA  
 399 curves, which clearly show the glass transition temperature  $T_g$  and exothermic  
 400 processes. The glass transition  $T_{g,onset}$ , the first exothermic process onset  $T_{exo1,onset}$  and  
 401 peak position  $T_{exo,peak}$  temperatures as well as glass stabilities  $S_1$ ,  $S_2$  for all glasses are  
 402 listed in Table 3. The glass stability is an often-used indicator describing the resistance  
 403 of glass to crystallization during heating. It is typically expressed by the difference  
 404 between the first crystallization onset value and the glass transition temperature  $S_1 =$   
 405  $T_{exo1, onset} - T_{g,onset}$  [46], or the first exothermic peak position and glass transition  
 406 temperature  $S_2 = T_{exo1, peak} - T_{g,onset}$  [47].

407

408 **Table 3** Thermal properties of glasses  $x\text{N(Li)NaBe}$ :  $T_{g, onset}$ ,  $T_{exo, onset}$ ,  $T_{exo, peak}$ ,  $S_1$ ,  $S_2$ ; obtained from DTA  
 409 spectra. For comparison, the thermal properties values are included for glasses  $35\text{M}_2\text{O}-65\text{SiO}_2$  and  
 410  $35\text{M}_2\text{O}-5\text{BeO}-60\text{SiO}_2$  from ref. [5].

ID	$T_{g, onset}$ (°C) +/- 2%	$T_{exo1, onset}$ (°C) +/- 2%	$T_{exo1, peak}$ (°C) +/- 2%	$S_1$ (°C) +/- 4%	$S_2$ (°C) +/- 4%
0Na	484	746	788	262	304
0NaBe	507	736	786	229	279
1NNaBe	497	835	852	338	355
2NNaBe	498	830	856	332	358



3NNaBe	508	892	917	384	409
4NNaBe	517	895	909	375	392
5NNaBe	516	930	966	414	450
0LiNa	431	689	712	258	281
0LiNaBe	456	663	726	207	270
1NLiNaBe	447	743	793	296	346
2NLiNaBe	446	-	789	-	343
3NLiNaBe	458	-	821	-	363
4NLiNaBe	470	832	854	362	384
5NLiNaBe	473	847	848	374	375

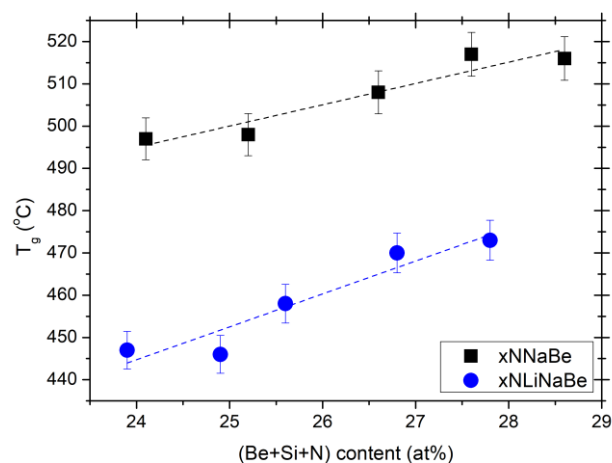
411

412 Firstly, let us discuss the glass transition  $T_g$  results for the xN(Li)NaBe glass series.  
 413 The  $T_g$  for 1NNaBe and 2NNaBe (~497 °C) as well as for 1NLiNaBe and 2NLiNaBe  
 414 (~447 °C) glasses have similar values, while it increases with further addition of Si<sub>3</sub>N<sub>4</sub>.  
 415 The observed difference between 1NNaBe and 5NNaBe glass is ~20 °C and between  
 416 1NLiNaBe and 5NLiNaBe glass it is ~26°C. Figure 6 presents the glass transition  
 417 temperature as a function of the summed Be+Si+N levels for all studied glasses. This  
 418 kind of property ( $T_g$ ) versus composition (Be+Si+N) presentation takes into account all  
 419 elements which contribute to the cross-linking of the glass network. Specifically, BeO  
 420 acting as intermediate glass-forming oxides will participate in the glass network with  
 421 [BeO<sub>4/2</sub>]<sup>2-</sup> tetrahedra, which are inserted in the network and strongly cross-link the  
 422 silicate units through Si-O-Be bridges, thus causing the increase in  $T_g$  [5]. When  
 423 nitrogen is chemically bonded to the silicon in the glass network as it substitutes for  
 424 oxygen, a stiffer, more cross-linked network ensues due to its three-fold coordination.  
 425 As observed in Fig. 6, an almost linear increase of  $T_g$  with Be+Si+N content is  
 426 demonstrated for both glass series. However, since the Be content is almost constants  
 427 for all glasses, the observed increase can mostly be attributed to different N and Si  
 428 levels (both Si and N increase as Si<sub>3</sub>N<sub>4</sub> is added to each glass series). It is also  
 429 apparent that  $T_g$  results for glasses xNLiNaBe, in which 9 mol% of Na<sub>2</sub>O was replaced  
 430 by Li<sub>2</sub>O, exhibit lower glass transition temperatures than the corresponding glasses  
 431 containing sodium only (xNNaBe). The same trend was observed for glasses prepared  
 432 in air [5]. Interestingly, the glass 0BNL has even a lower  $T_g$  than for the binary 34Li<sub>2</sub>O-  
 433 66SiO<sub>2</sub> glass (456 °C, [48]), despite the 1 mol% higher modifier content in our 0NLBe  
 434 glass. The much lower crosslinking capability of lithium ions compared to sodium ions

435 in silicate glasses seems to be compensated by a mixed modifier effect. Thus, the  $T_g$   
436 decreases even more for the mixed compared to the pure Li-glass.

437 Results obtained for the  $xN(Li)NaBe$  glass series were compared with N-free  
438 (0NaBe and 0LiNaBe) and also Be-free (0Na and 0LiNa) glasses [5]. First, we discuss  
439 the changes in thermal behavior observed as a result of Be and N doping for the  
440  $xN(Li)NaBe$  glass series. The increase of  $T_g$  observed as a result of doping 0LiNa glass  
441 with BeO is  $\sim 16$  °C or  $\sim 25$  °C, found for 1N(Li)NaBe and 0NaBeLi glasses, respectively.  
442 The higher value for 0NaBeLi can be attributed to additional  $Al^{3+}$  ( $\sim 2.5$  at%). However,  
443 the  $T_g$  of 4N(Li)NaBe and 5N(Li)NaBe glasses is higher even than that of 0LiNaBe; their  
444  $T_g$  values increase by  $\sim 40$  °C when compared to the undoped glass 0LiNa. Based on  
445 these results for the  $xN(Li)NaBe$  glass series, it can be assumed that addition of  $\sim 1.6$   
446 %at of Be increases the  $T_g$  by  $\sim 16$  °C, and further addition of 2 at% of Al increases  $T_g$   
447 by another  $\sim 9$  °C. A similar increase is observed when doping the Al-free glasses with  
448  $\sim 2$  at% of N. The highest increase in  $T_g$  (up to  $\sim 26$  °C), is seen for the incorporation of  
449  $\sim 3.4$  at% of N. A similar behavior is also observed for the  $xNNaBe$  glass series.  
450 Interestingly, a higher slope is observed in Fig. 6 for glasses  $xN(Li)NaBe$  than glasses  
451  $xNNaBe$ . This result may be due to the higher content of N, which was detected by  
452 SEM-EDS for glasses 3N(Li)NaBe, 4N(Li)NaBe and 5N(Li)NaBe.

453



454

455 **Figure 6** The dependence on the analyzed Be+Si+N content for  $T_{g, onset}$  values for glasses  
456  $xNNaBe$  and  $xN(Li)NaBe$  studied in this work. Lines between data points show trends of  $T_g$  - and  
457 are given as guides for the eyes only.

458

459 Table 3 depicts also the thermal glass stability ( $S_1$  and  $S_2$ ) for all glasses  
460  $xN(Li)NaBe$ . It is evident that all  $xNNaBe$  and  $xN(Li)NaBe$  glasses show higher values  
461 of  $S$  than their reference glasses [5]. Moreover, glasses doped with lithium ( $xN(Li)NaBe$ )  
462 show in general lower values of thermal stability than the corresponding glasses  
463 containing only sodium ( $xNNaBe$ ), similarly to  $T_g$  values. In our previous work [5], we  
464 have shown that beryllium addition decreases the glass stability in both Na-Al-Si-O and  
465 Li-Na-Al-Si-O glass systems in approximately a monotonic way. Contrary to Be doping,  
466 this work shows that an increase in the contents of both N and Si increases glass  
467 stability as observed for phosphate glasses [28]. Based on this knowledge we can  
468 assume that Al which is present in  $0(Li)Na$  and  $0(Li)NaBe$  glasses has an analogous  
469 effect as Be addition on the  $S$  value. The strongest influence of N incorporation into  
470 the silicate network is observed for glasses  $5NNaBe$  and  $4N(Li)NaBe$ , and this is in  
471 accordance with the estimated N content (see Table1).

472

## 473 Conclusions

474 Two different glass series with nominal composition close to  $35M_2O-5BeO-(60-$   
475  $x)SiO_2-xSi_3N_4$ , where M is Na or Na+Li and  $SiO_2$  was substituted by up to 5 mol%  
476  $Si_3N_4$ , were prepared in this work. All materials were found to be X-ray amorphous  
477 while the topography and composition of their cross-sections were homogenous and  
478 reproducible. All glasses were found to contain N, the content of which is highest for  
479 glasses doped with 5 mol% of  $Si_3N_4$ .

480 The results of Raman spectroscopy showed a high degree of spectral overlap  
481 between the studied glasses. Both glass series have silicate networks made up entirely  
482 of  $Q^3$  and  $Q^2$  silicate units, with higher content of  $Q^2$  groups than in the analogous N-  
483 and Be-free silicate glasses. This difference can be attributed to the incorporation of  
484  $[BeO_{4/2}]^{2-}$  tetrahedra. A slight decrease in the  $Q^2$  fraction is observed with  $Si_3N_4$   
485 addition, since this increases the network former to network modifier ratio. For the glass  
486  $5N(Li)NaBe$ , with the highest confirmed nitrogen content, the  $Q^2$  signature is still high,  
487 but at the same time there is evidence for the formation of  $Q^4$  units; thus, confirming  
488 the higher degree of network polymerization upon  $Si_3N_4$  addition. Since three-fold  
489 bonded nitrogen substitutes for two-fold coordinated bridging oxygen atoms, a  
490 transformation of  $Q^n$  oxide species into  $Q^{n+1}$  oxy-nitride species is expected. In the  
491 case of  $5N(Li)NaBe$ , disproportionation of  $Q^3$  groups into  $Q^4$  and  $Q^2$  units was found to  
492 occur.



493 An increase in glass transition temperature is found for all (Li)-Na-Si-O glasses after  
494 doping with beryllium and incorporation of silicon and nitrogen into the silicate network.  
495 An increase in  $T_g$  (up to  $\sim 26$  °C for Li-Na-Be-Si-O-N glass series) is observed as a  
496 result of Si and N incorporation. The incorporation of N also increases significantly the  
497 thermal stability of glasses.

498

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509

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