

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 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 Si^{4+} ($\alpha_{\text{Si}^{4+}} = 0.033 \text{ \AA}^3$) [1]. 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 Al_2O_3 , that can act as network
43 modifier when 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 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 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 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 Si_3N_4
109 (ChemPur GmbH), BeO (99% Alfa Aesar), SiO_2 (99.99% ChemPur GmbH), Na_2CO_3
110 (99.9+% ChemPur GmbH) and Li_2CO_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 Si_3N_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 H_2O , 0.5 ml of HF acid and 5 ml of 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 N₂ gas and oxygen
137 contents from infrared absorption of CO₂ 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 10⁻⁴ 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_{<3}).

166



167 *2.2.4. Raman spectroscopy*

168 Raman spectra were obtained in the range from 100 to 2000 cm^{-1} with a resolution
169 of 2 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 μm in diameter. Spectra have been normalized to the intensity
172 of the high frequency envelop at about 1090 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 Al_2O_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 Si_3N_4 resulted in dark-grayish, shiny and translucent glass samples. The
192 samples become less shiny and translucent with an increase in Si_3N_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].

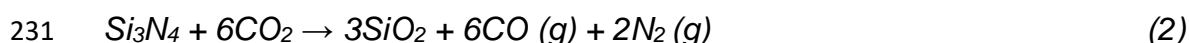
196 The target and analyzed compositions of the (Li)-Na-Be-Si-O-(N) glass series are
197 listed in Table 1. Samples IDs are based on the nominal $x\text{Si}_3\text{N}_4$ quantity in mol% ($x =$
198 1, 2, 3, 4 or 5) and suggest glass series with sodium ($x\text{NNaBe}$) or sodium and lithium

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 Si₃N₄) to ~3.4 at% for glasses doped with 5 mol% of Si₃N₄.
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 CO₂ (carbonate) in the raw materials,
227 which during release acts against N incorporation into the glass network [24]. This is
228 due to CO₂ from carbonates which may oxidize Si₃N₄ according to the reactions:



232



233 leading to N₂ loss. Also, Si₃N₄ 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 Si₃N₄
 239 releasing N₂ 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 35M₂O–65SiO₂ and 5BeO–35M₂O–60SiO₂ taken from ref.[5].

Sample ID	Target composition (in at%)	SEM-EDS (in at%)	ICP-OES (in at%)
35Na₂O–5BeO–(60-x)SiO₂–xSi₃N₄			
1NNaBe	Na _{24.4} Be _{1.7} Si _{20.2} O _{52.3} N _{1.4}	Na _{22.3} Be _{1.7} Si _{21.0} O _{54.9} N _{<3}	Na _{23.6} Be _{1.8} Si _{21.4} O _{52.3} N _{0.9}
2NNaBe	Na _{23.1} Be _{1.7} Si _{21.1} O _{51.5} N _{2.6}	Na _{26.8} Be _{1.5} Si _{18.9} O _{52.8} N _{<3}	Na _{23.2} Be _{1.8} Si _{22.0} O _{51.5} N _{1.4}
3NNaBe	Na _{22.8} Be _{1.6} Si _{21.5} O _{50.2} N _{3.9}	Na _{26.2} Be _{1.5} Si _{19.3} O _{53.1} N _{<3}	Na _{23.1} Be _{1.7} Si _{22.8} O _{50.2} N _{2.1}
4NNaBe	Na _{22.5} Be _{1.6} Si _{21.9} O _{48.9} N _{5.1}	Na ₂₄ Be _{1.5} Si _{20.3} O _{54.2} N _{<3}	Na _{23.5} Be _{1.8} Si _{22.8} O _{48.9} N ₃
5NNaBe	Na _{22.2} Be _{1.6} Si _{22.2} O _{47.6} N _{6.3}	Na _{22.2} Be _{1.5} Si _{21.2} O ₅₅ N _{<3}	Na _{23.8} Be _{1.8} Si _{23.6} O _{47.6} N _{3.2}
9Li₂O–27Na₂O–5BeO–(59-x)SiO₂–xSi₃N₄			
1NLiNaBe	Li ₆ Na _{18.7} Be _{1.7} Si _{20.4} O _{52.5} N _{1.3}	Li _{5.8} Na _{19.2} Be _{1.8} Si _{19.7} O _{53.6} N _{<3}	Li _{6.8} Na _{16.8} Be _{1.8} Si _{21.2} O _{52.5} N _{0.9}
2NLiNaBe	Li _{5.9} Na _{17.8} Be _{1.7} Si _{20.8} O _{51.2} N _{2.6}	Li _{5.5} Na _{20.5} Be _{1.5} Si _{19.3} O _{53.1} N _{<3}	Li _{6.9} Na _{16.9} Be _{1.8} Si _{21.6} O _{51.2} N _{1.5}
3NLiNaBe	Li _{5.9} Na _{17.6} Be _{1.6} Si _{21.2} O _{49.8} N _{3.9}	Li _{5.2} Na _{19.9} Be _{1.4} Si _{18.6} O _{53.1} N _{3.6}	Li _{6.9} Na _{17.5} Be _{1.8} Si _{21.8} O _{49.8} N ₂
4NLiNaBe	Li _{5.8} Na _{17.4} Be _{1.6} Si _{21.5} O _{48.6} N _{5.1}	Li _{4.7} Na _{21.8} Be _{1.3} Si _{17.5} O _{49.5} N _{5.2}	Li ₇ Na _{17.6} Be _{1.8} Si _{22.1} O _{48.6} N _{2.9}
5NLiNaBe	Li _{5.7} Na _{17.1} Be _{1.6} Si _{21.9} O _{47.3} N _{6.3}	Li _{4.8} Na _{19.6} Be _{1.3} Si _{18.6} O _{50.7} N ₅	Li _{7.1} Na _{17.9} Be _{1.9} Si _{22.5} O _{47.3} N _{3.4}
35M₂O–65SiO₂ and 35M₂O–5BeO–60SiO₂ [5]			
0Na	Na _{23.3} Si _{21.7} O ₅₅	Na _{19.2} Al _{0.5} Si _{23.3} O ₅₇	Na _{22.4} Si _{21.1} Al _{0.5} O ₅₆
0NaBe	Na _{23.7} Be _{1.7} Si _{20.3} O _{54.2}	Na _{15.5} Be _{1.9} Al _{1.1} Si _{23.3} O _{58.1}	Be _{1.8} Na _{20.7} Si _{20.6} Al _{0.8} O _{56.2}
0LiNa	Li ₆ Na ₁₈ Si _{21.3} O _{54.7}	Li _{5.8} Na _{18.4} Al _{0.5} Si _{20.8} O _{54.5}	Li _{6.7} Na ₁₇ Si _{21.3} Al _{0.4} O _{54.6}
0NaBeLi	Li _{6.1} Na _{18.3} Be _{1.7} Si ₂₀ O _{53.9}	Li ₆ Na _{14.7} Be _{1.8} Al _{2.5} Si _{19.8} O _{55.3}	Li ₈ Na _{16.6} Be _{1.7} Si ₁₇ Al _{2.8} O _{53.9}

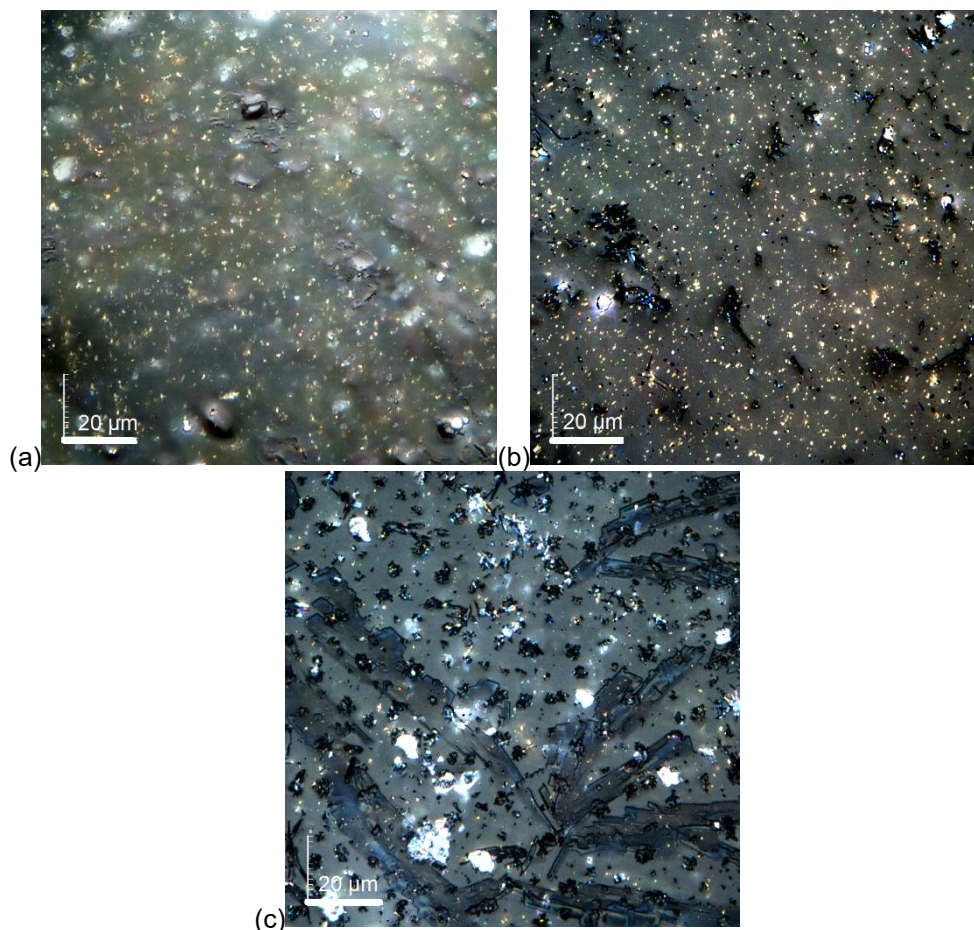
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245 Figure 1(a) presents the CSLM image for glass 4NNaBe. Its topography looks
 246 like a typical glass surface [38]. The other glasses of the xNNaBe series show a similar
 247 glossy topography with grayish color. The topography of glass 1NLiNaBe 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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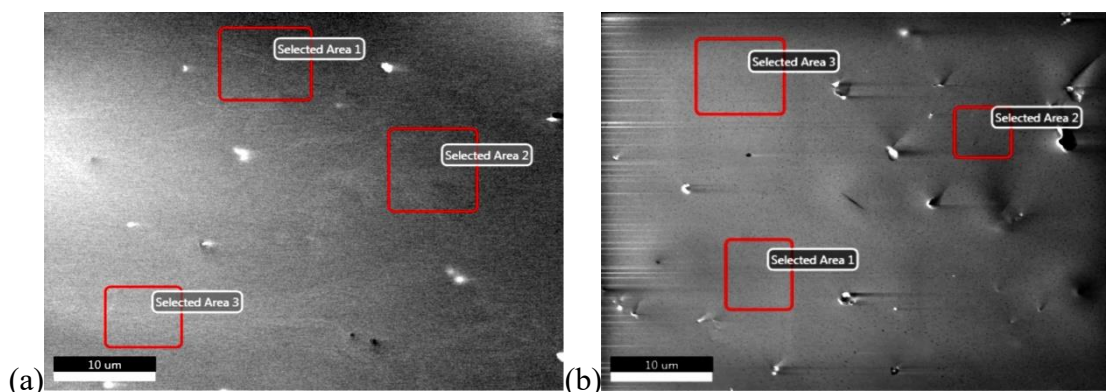
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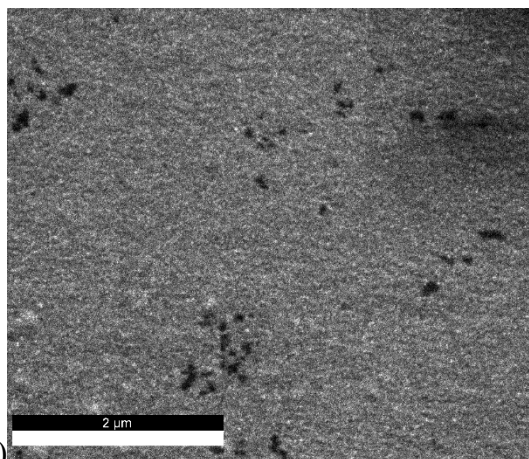
Figure 1 CSLM micrographs of glasses surfaces: (a) 4NNaBe, (b) 1NLiNaBe and (c) 5NLiNaBe.

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

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268 **Figure 2** SEM micrographs for fractured glasses: (a) 3NNaBe, (b) 4NLiNaBe and (c) 1NNaBe (with
269 higher magnification).
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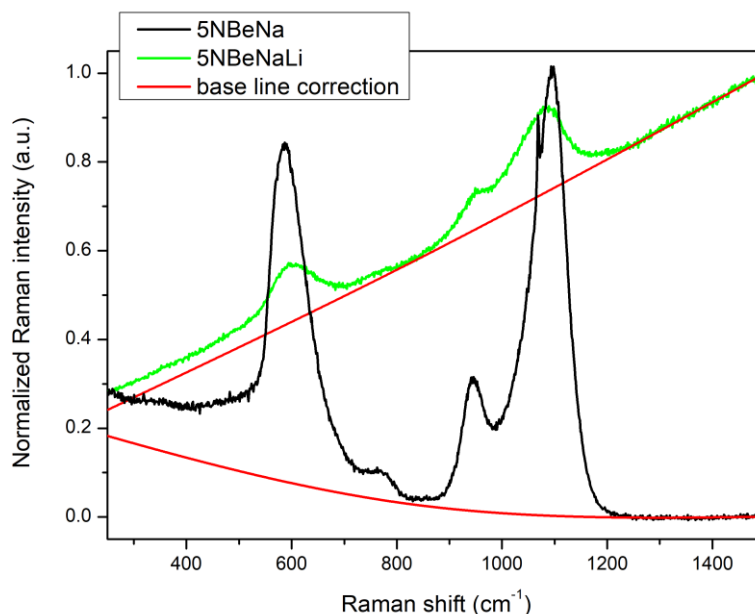
271 **3.2. Vibrational spectroscopy**

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 5BeO-
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.

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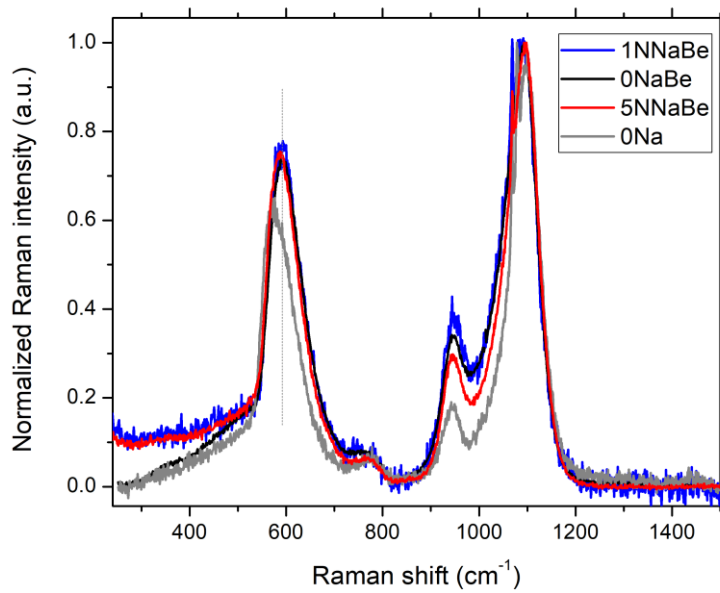
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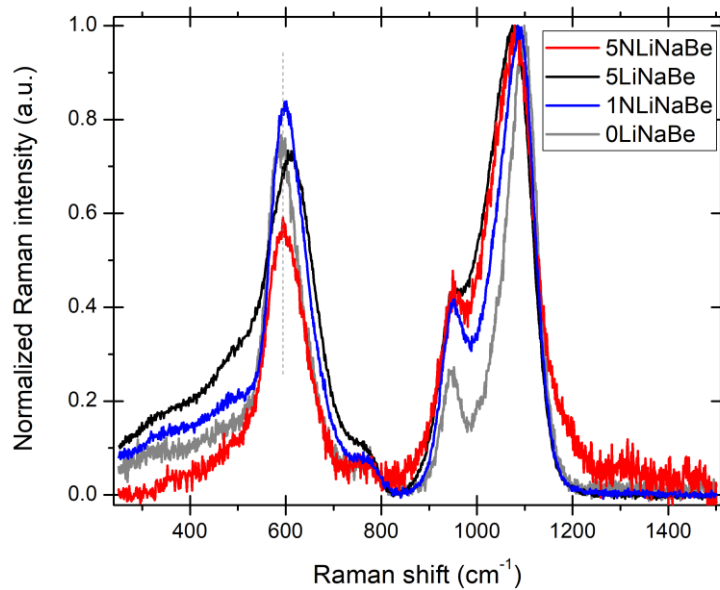
283
 284 **Figure 3** Raman spectra for exemplar glasses 5NNaBe and 5NLiNaBe, measured using the 633 and
 285 514.5 nm laser excitation lines, respectively. These spectra are not baseline corrected, but adjusted in
 286 their intensities for better comparison (red lines give examples for base line subtraction 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 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 35Na₂O-65SiO₂ (0Na) and 35M₂O-5BeO-60SiO₂ (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⁻¹.

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 cm^{-1} band, reflecting the
317 presence of Q^2 groups (ca. 950 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 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 Al_2O_3 substitution for 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 Na^+ and/or 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 Al_2O_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 Al_2O_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 Li_2O content, while the content of BeO is lower
338 than the BeO and Al_2O_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

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

344 In both the $x\text{N}(\text{Li})\text{NaBe}$ 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 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 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 Si_3N_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.

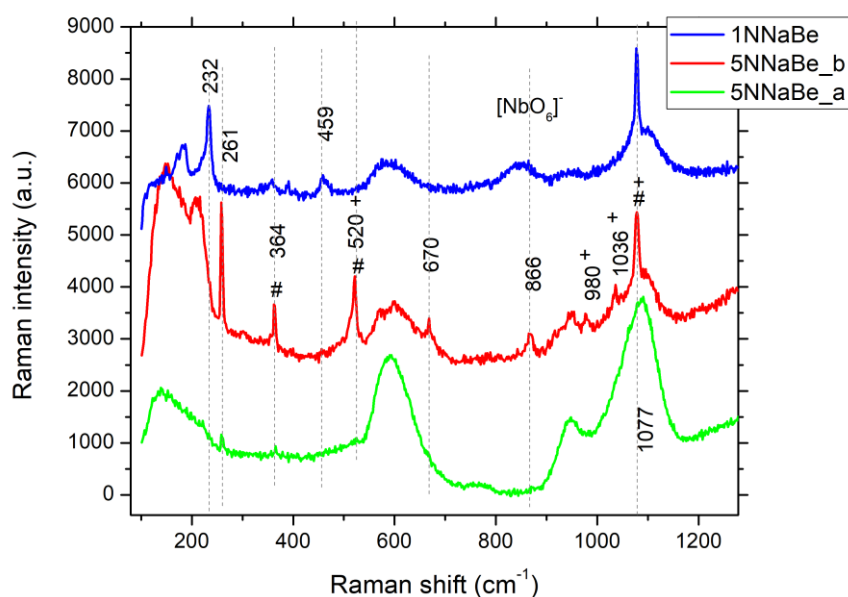
363

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

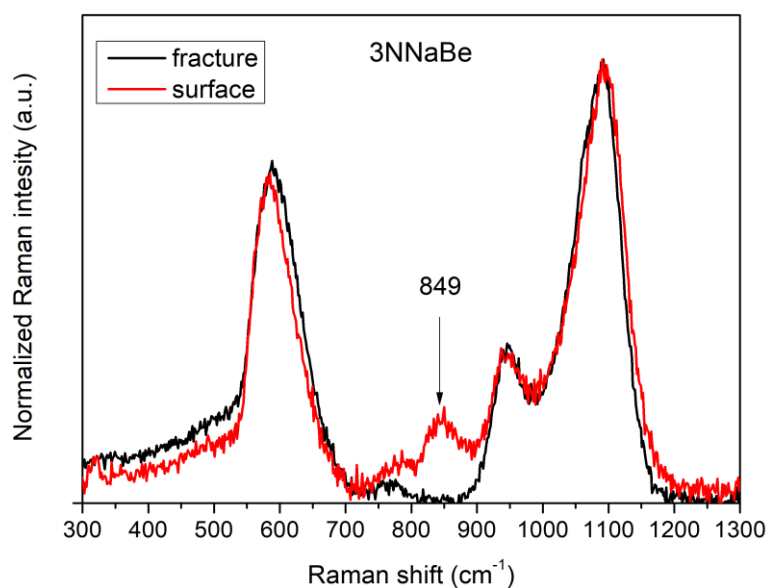
365 While measuring the spectra of N-containing glasses, by focusing the Raman
366 microscope on vitreous areas of the samples, we noticed the presence of some
367 crystalline inclusions and impurities from the niobium crucibles. As an example, Figure
368 5a shows the Raman spectra of such heterogeneous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

373





(a)



(b)

Figure 5 (a) Raman spectra of heterogeneous spots for glasses 1NNaBe and 5NNaBe and (b) Raman spectra of glass 3NNaBe measured on a fresh cross-section (black) and the surface (red) which was in contact with the Nb crucible. Sharp bands in (a) marked with # and + indicate the 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 using the 633 nm laser excitation line.

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

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384 surface exhibits an additional band at $\sim 849\text{ cm}^{-1}$ which can be assigned to highly
 385 distorted 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 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

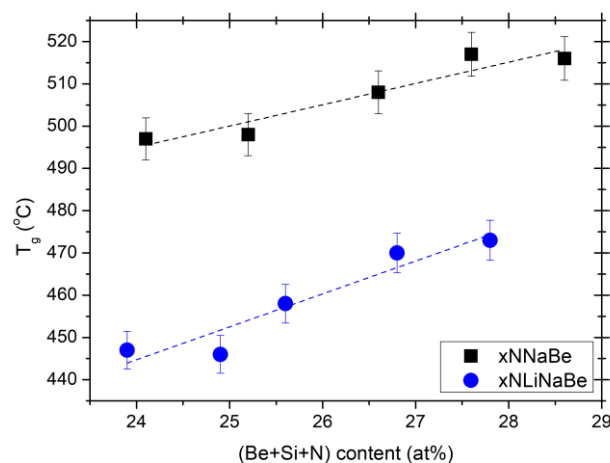
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412 Firstly, let us discuss the glass transition T_g results for the xN(Li)NaBe glass series.
413 The T_g for 1NNaBe and 2NNaBe (~497 °C) as well as for 1NLiNaBe and 2NLiNaBe
414 (~447 °C) glasses have similar values, while it increases with further addition of Si₃N₄.
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_{4/2}]²⁻ 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 Si₃N₄ is added to each glass series). It is also
429 apparent that T_g results for glasses xNLiNaBe, in which 9 mol% of Na₂O was replaced
430 by Li₂O, 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 34Li₂O-
433 66SiO₂ 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 ~ 16 °C or ~ 25 °C, found for 1N(Li)NaBe and 0NaBeLi glasses, respectively.
442 The higher value for 0NaBeLi can be attributed to additional Al^{3+} (~ 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 ~ 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 ~ 1.6
446 %at of Be increases the T_g by ~ 16 °C, and further addition of 2 at% of Al increases T_g
447 by another ~ 9 °C. A similar increase is observed when doping the Al-free glasses with
448 ~ 2 at% of N. The highest increase in T_g (up to ~ 26 °C), is seen for the incorporation of
449 ~ 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 $xNLiNaBe$ glasses show higher values
461 of S than their reference glasses [5]. Moreover, glasses doped with lithium ($xNLiNaBe$)
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 $4NLiNaBe$, 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 $5NLiNaBe$, 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 $5NLiNaBe$, 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 ~ 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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