From network depolymerization to stress corrosion cracking in sodium-borosilicate glasses: Effect of the chemical composition
Marina Barlet, Jean-Marc Delaye, Bruno Boizot, Daniel Bonamy, Richard Caraballo, Sylvain Peuget, Cindy Rountree

To cite this version:

HAL Id: cea-01483763
https://hal-cea.archives-ouvertes.fr/cea-01483763
Submitted on 6 Mar 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
From network depolymerization to stress corrosion cracking in sodium-borosilicate glasses: Effect of the chemical composition

Marina Barlet a, Jean-Marc Delaye b, Bruno Boizot c, Daniel Bonamy a, Richard Caraballob, Sylvain Peuget b, Cindy L. Rountree a,*

a SPEC, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette, France
b CEA, DEN, DTCD, SCLP, Marcoule, France
* LSI, École Polytechnique, CEA, CNRS, Université Paris-Saclay, 91128 Palaiseau, France

A R T I C L E   I N F O

Article history:
Received 20 May 2016
Received in revised form 7 July 2016
Accepted 14 July 2016
Available online 12 August 2016

Keywords:
Stress corrosion cracking
Sodium borosilicate glass
Fracture

A B S T R A C T

The study herein examines how chemical composition impacts sub-critical stress corrosion cracking (SCC) in sodium borosilicate glasses. The crack speed versus stress intensity factor (v vs. KI) curves were obtained for seven ternary SiO2-Na2O-B2O3 (SBN) glasses of selected chemical compositions. Na2O plays an interesting role in the SCC behavior. First, increasing the Na2O concentration yields an increase in the environmental limit (Kc). Second, increasing the Na2O concentration affects how fast SCC occurs as Kc increases (i.e. the slope in region I SCC). This second effect is highly nonlinear: it is insignificant for Na2O <20% but it becomes increasingly important above 20%, when sodium acts as a network modifier. Raman spectroscopy and Molecular Dynamics (MD) simulations aid in revealing the structural variations which arise from increasing concentrations of Na2O. Na2O causes the relative proportions of the different chemical bonds accessible in SBN glasses to vary. For this series of glasses, the Si-O-Si bond does not dominate the SCC properties. SCC variations originate in the mesoscale structure where sodium ions act as network modifiers on both the silica and borate units, thus yielding a partial depolymerization (i.e. a decrease in the reticulation level) of the network. This second effect reveals itself to be the one responsible for the SCC chemical dependency. Poisson’s ratio increases approximately linearly with increasing Na2O concentration, and thus, it is also not simply proportional to the slope in region I SCC. Partial depolymerization of the glass provides a novel prospective on the controlling factors in the sub-critical crack growth.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Stress-corrosion cracking is a phenomenon by which water (or other environmental factors) aids in the slow propagation of pre-cracks/flaws in materials. This slow propagation gains speed untimely leading to the overall failure of the material. This is one of the reasons why glass walkways (e.g. London Bridge, Grand Canyon, Yuntaishan Sky Walkway, Eiffel Tower…) have sacrificial protective glass panels which are removed when flaws are visible. In the absence of a corrosive environment, the stress intensity factor (i.e. stress felt by the crack front, KI) must exceed the material’s fracture toughness (Kc) for a crack front to propagate [1–3]. Yet, within a corrosive environment, water molecules attack the stretched network at the crack tip causing sub-critical crack propagation (i.e. KI<Kc).

In general, three regions exist in the sub-critical cracking domain (Fig. 1). In region I, the crack front velocity, v, depends on the chemical reactions rates at the crack tip. In region II, the crack front velocity depends on the time for the water to reach the crack front. In region III, the crack front moves too fast for water to reach the crack front [1,4]. Occasionally, a fourth region, region 0 or the environmental limit (Kc), exists. Kc defines a threshold limit below which a crack front will not propagate.

Efforts to relate the SCC v as a function of KI to the glass’s chemical composition remain rather rudimentary as glasses are far too complex for a comprehensive analysis based on a rather small number of samples [1–5]. In these studies [1–5], a continuing hypotheses persists that the rupture of the Si-O-Si bond and/or the reaction rate theory control the SCC dynamics in region I [1–3]. This paper puts this hypothesis to test in SiO2-Na2O-B2O3 (SBN) glasses. Moreover, it will overturn this hypothesis for the SBN series and shows that the depolymerization (the amount of reticulation in the glass network) controls the sub-critical crack propagation.

This paper should be seen as the third in a series, the first two being Barlet et al. 2013 [6] and 2015 [7]. Ternary SBN glasses provide a simple model glass to examine the importance of a glass’s chemical composition on its mechanical response in region 0 and I. Glasses herein contain two network formers (SiO2 and B2O3) and one network modifier (Na2O). These three components represent the major components for many industrial glasses; yet, little is known about how the chemical composition alters the stress corrosion cracking (SCC) properties. This paper examines v versus KI curves for regions 0 and I for seven ternary glasses: E-mail address: cindy.rountree@cea.fr (C.L. Rountree).
SiO₂⁻Na₂O⁻B₂O₃ (SBN) glasses. Herein, $K_e$ clearly shifts to higher environmental limits when Na₂O increases. On the other hand, SBN glasses display an increasing susceptibility to water as Na₂O increases [8] as evidenced by an increasing slope in region I. These results highlight Na₂O role on the mechanical behavior of glasses. Furthermore, they depend on Na₂O’s role in the glass: network modifier or network charge compensator. Results herein reveal the depolymerization of the glass providing an indication of the stress corrosion cracking behavior in region I. These findings provide a new prospective on the controlling factors in sub-critical crack growth.

2. Methods

Barlet et al. 2013 [6] and 2015 [7] directly concern the series of SBN glasses presented herein and should be regarded as precursors to this paper. Most experimental and numerical protocols invoked in this study have been extensively tested and reported elsewhere. Thus, this section briefly reviews experimental and numerical protocols and references detailed works for further readings. The first Subsection 2.1 details the chemical composition of the 7 SBN glasses and recalls the standard way to characterize them. Subsection 2.2 describes fracture tests used to characterize the stress corrosion cracking (SCC) behavior. Subsection 2.3 details the spectroscopy tests used to analyze and characterize the structure of the glass. Subsection 2.4 recalls methods to acquire density, Poisson’s ratio, and the Young’s modulus. Researchers manually collected and logged temperature and humidity measurements. SCC experiments lasted from 1 week to 1 month. In order to limit temperature and humidity variations during a single experiment, SCC runs occur with no direct contact with the outside. The average yearly temperature and humidity in the chamber was 30±5°C and 40±10%RH. Appendix A provides an indication of the average temperature and humidity during each experiment.

2.1. Glass chemical composition

Glass fabrication invokes the same procedure as previously reported by the coauthors [6,7]. Table 3 recalls the target chemical composition of each glass [6]. A third party (PrimeVerre) verifies the glass chemical compositions via SEM-EDS (Environmental Scanning Electron Microscope coupled with an Energy Dispersive Spectrometer) and/or ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy). SEM-EDS results revealed small amounts of impurities, <0.5%. Results reported herein are from ICP-AES measurements and have an uncertainty of 10%. Previous works by the co-authors examined and reported the chemical composition of the glasses along with their densities, glass structure, and hardness [6,7,9–11]. When possible, the same batch was used here as in the previous papers.

Table 1 recalls the measured ICP-AES, $K_{BSN} (\frac{Na_2O}{SiO_2})$ where [·] = mol% [6], $R_{BSN} (\frac{Na_2O}{SiO_2})$, and density ($\rho$) presented in [6,7]. Sample classification herein concerns two $K_{BSN}$ groupings: 2.52 ± 0.03 (blue series) and 4.6 ± 0.12 (red series). Grouping glasses via their $K_{BSN}$ value provides a constant mol % ratio between [SiO₂] and [B₂O₃]. A secondary parameter is used in categorizing the glasses: $R_{BSN} = \frac{Na_2O}{SiO_2}$. Authors invoke the $R_{BSN}$ and $K_{BSN}$ parameters as they aid in estimating elementary units (BO₃ planar units, BO₄ tetrahedral, Metaborate units, pyroborate units, Silica tetrahedral with $i$ (i = 1 to 4) bridging oxygen atoms) [6,12–14] and some macroscopic properties [7,13,15]. Thus, this notation will be continued herein.

2.2. SCC experimental set-up

SCC techniques invoke a well-documented procedure [16–20] which require DCDC (Double Cleavage Drilled Comparison) sample geometry (5 × 25 mm² rectangular parallelepiped with a 1 mm diameter hole which passes through the 5 × 25 mm² faces). This geometry provides a decreasing $K_e$ as the crack length grows [21,22]. Literature exemplifies stable crack propagation in region 0 and I for DCDC samples [23]. Pallares et al. [21] provides an updated version of He et al. [22] equation to calculate the stress intensity factor ($K_I$) at the crack tip based on the length of the crack (c):

$$K_I = \left( a_0 + a_1 \frac{w}{r} + a_2 \frac{w^2}{r} \right)^1/2 + \left( a_3 + a_4 \frac{w}{r} + a_5 \frac{w^2}{r} \right)^1/2 \times \frac{C}{r}$$

where $\sigma = \frac{F}{A}$ is the stress applied to the sample, $A$ is the surface area where the force $F$ is applied, $r$ is the radius of the cylindrical hole, $w$ is the width of the specimen, and $a_0$ (j = 0 to 5) are fitting parameters. Pallares et al. [21] calculated the following fitting parameters with Finite Element simulations for Eq. (1): $a_0 = 0.3156$, $a_1 = 0.7350$, $a_2 = 0.0346$, $a_3 = -0.4093$, $a_4 = 0.3794$, and $a_5 = -0.0257$. A Deben compression machine applies the force on the 5 × 25 mm² facets. Initially, the applied force increases slowly until two precracks initiate off the hole. The cracks are then allowed to stabilize. Subsequently, the force is set and a tubular microscope coupled with Matlab programs images the crack front’s displacement with the applied forces (see Fig. 2 for typical images) continuously. SCC runs occur with no direct control of the temperature nor humidity (i.e. ambient conditions). Researchers manually collected and logged temperature and humidity measurements. SCC experiments lasted from 1 week to 1 month. In order to limit temperature and humidity variations during a single SCC experiment, experiments are conducted in a chamber with limited contact with the external environment. The chamber was located in a room which rests underground and within the center of the building (i.e. none of the walls had direct contact with the outside). The average yearly temperature and humidity in the chamber was 30±5°C and 40±10%RH. Appendix A provides an indication of the average temperature and humidity during each experiment.

Post-image analysis provides the $\nu$ versus $K_e$ curves. When calculating the slope in region I, from time to time, outliers occur. These outliers are discarded in the slope calculations. Errors in slopes represent uncertainty obtained from fitting the points.

2.3. Structural characterization of the glass network

Barlet et al. [7] presents $^{11}$B magic angle spinning (MAS) nuclear magnetic resonance (NMR) experimental methods and results for the SBN samples. Table 1 recalls the measured $^{11}$B MAS NMR ratios of $^{11}$B (amount of 4-coordinated boron), $^{11}$B (amount of 3-coordinated boron) and presented in [6,7]. Post-analysis of $^{11}$B MAS NMR gives...
Table 1
Correlations between chemical compositions and other mechanical properties of SBN glasses. Chemical compositions come from measured ICP-AES (Inductively coupled plasma atomic emission spectroscopy) values where [ ] mol%. These measurements have an uncertainty of 10%; thus target values (Table 3) are within the uncertainties of measured values. The table also contains other information on structural and physical properties of the glasses: \(K_{\text{BSN}}\) (mol% of \(\text{Na}_2\text{O}\)), density \(\rho\), and \(^{10}\)B MAS NMR ratios of \(^{10}\)B (amount of 4-coordinated boron) and \(^{11}\)B (amount of 3-coordinated boron) [6,7], an estimate of the amount of \([\text{Na}_2\text{O}]\) causing NBO in the glasses (Maugis’s model [86]) for each SBN glass.

<table>
<thead>
<tr>
<th>Glass</th>
<th>([\text{SiO}_2])</th>
<th>([\text{Na}_2\text{O}])</th>
<th>([\text{B}_2\text{O}_3])</th>
<th>(K_{\text{BSN}})</th>
<th>(\rho) (g/cm(^3))</th>
<th>(E) (GPa)</th>
<th>(\nu)</th>
<th>(\beta_s)</th>
<th>n</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBN12</td>
<td>59.6%</td>
<td>16.5%</td>
<td>23.9%</td>
<td>2.5</td>
<td>0.69</td>
<td>60%</td>
<td>40%</td>
<td>2.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBN30</td>
<td>51.0%</td>
<td>28.9%</td>
<td>20.1%</td>
<td>2.5</td>
<td>1.4</td>
<td>68.9%</td>
<td>31.1%</td>
<td>15.7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBN35</td>
<td>46.9%</td>
<td>34.5%</td>
<td>18.6%</td>
<td>2.5</td>
<td>1.9</td>
<td>62.2%</td>
<td>37.8%</td>
<td>24.9%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBN70</td>
<td>70.0%</td>
<td>14.2%</td>
<td>15.8%</td>
<td>4.4</td>
<td>0.9</td>
<td>72%</td>
<td>28%</td>
<td>2.8%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBN63</td>
<td>66.7%</td>
<td>19.2%</td>
<td>14.1%</td>
<td>4.7</td>
<td>1.4</td>
<td>81%</td>
<td>19%</td>
<td>8.0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBN59</td>
<td>61.1%</td>
<td>25.5%</td>
<td>13.3%</td>
<td>4.6</td>
<td>1.9</td>
<td>79.5%</td>
<td>20.5%</td>
<td>15.9%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SBN55</td>
<td>58.1%</td>
<td>29.1%</td>
<td>12.9%</td>
<td>4.5</td>
<td>2.3</td>
<td>76.3%</td>
<td>23.7%</td>
<td>20.5%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Raman measurements employ a YAG laser (\(\lambda = 532\) nm) on a JobinYvon HR800 spectrometer [9,11]. The laser has an adjustable output power in order to prevent significant heating of the samples. Results herein depict the average of ten measurements accumulated over 10 s. For the \(K_{\text{BSN}}\sim 2.5\), no clear baseline measurement was feasible within the data set due to the multiple vibrational responses. Hence, the \(K_{\text{BSN}}\sim 2.5\) spectra still contain the baseline. On the other hand, the \(K_{\text{BSN}}\sim 4.5\) series did display a similar baseline between the series, so the baseline was removed for data presented herein. Raman spectra merge several different vibrational modes. The interpretation of the co-authors herein relies on comparing and contrasting results found herein with literature [24–41].

2.4. Density, Poisson’s ratio and Young’s modulus

Barlet et al. [6] presents methods to acquire the density (\(\rho\)) of a sample using Archimedes principles (see [6] for detailed explanation). These samples were then used in Barlet et al. [7] for ultrasonic echography techniques. The tests use a 5 MHz piezoelectric transducers. Knowing the thickness of the sample (measured via digital micrometer with an accuracy of \(\pm 1\)\(\mu\)m) and the transit time, one can calculate the longitudinal \((V_L)\) and transverse \((V_T)\) ultrasonic velocities of acoustic waves. Using these values, the Young modulus \((E)\) and the Poisson’s ratio \((\nu)\) can be calculated:

\[
E = \rho \cdot \left( \frac{3 V_L^2 - 4 V_T^2}{V_T^2 - 1} \right)
\]

\[
\nu = \frac{V_L^2 - 2 V_T^2}{2 (V_L^2 - V_T^2)}
\]

Table 1 presents \(E\), \(\nu\) and \(\rho\) for the SBN samples.

2.5. MD simulations

Molecular Dynamics (MD) simulations provide researchers with the structural organization of ternary \(\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}\) glass systems. MD simulations herein use empirical interatomic potentials developed by Kieu et al. [42,43] for SBN glasses. These potentials incorporate Buckingham’s potential with Coulomb interactions via an Ewald sum [44], Guillot–Sator potential parameters describe the Si-O, Na-O and O-O interactions [45]. The parameters for the B-O interactions have been adjusted to fit density and elastic modulus properties on a large set of \(\text{SiO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}\) glasses. All the calculations invoke DL_POLY code [46].

Formation of the glassy network occurs by giving 1500 Si, B, O, and Na atoms random locations in a cube at 4000 K. The density of the systems was 5% lower than experimental densities in order to reach a final
density close to the experimental one. The system relaxation occurred over a period of 100 ps (time steps were 1 fs).

Subsequently, the glasses fabrication occurs via quenching the systems to 300 K at a rate of $5 \times 10^{12}$ K/s. A three step process occurs at this point in order to obtain the structure of the glasses. First, volume equilibration occurs via NPT calculation ($2 \times 10^5$ time steps). Second, holding the volume constant (determined by the previous step), NVE ensemble simulations enable the atoms to equilibrate around their equilibrium sites. This step occurs for 5000 time steps. Finally, the forces between the atoms are minimized via a steepest descent algorithm.

Structural averaging occurs on 11 configurations separated by 500 time steps. These 11 configurations come about after a steepest descent to 0 K and occur via an equilibration at 0 K. For each chemical composition, four independent trajectories improve the statistics. This process is repeated for all target compositions presented in Table 3. (Note: Barlet et al. [6] presents multiple simulated MD glasses.

Variables correspond to the types of atoms associated to O atoms. (e.g. SiB corresponds to oxygen atoms between a Si atom and a B atom. SiSiB corresponds to overcoordinated oxygen atoms with 2 Si atoms and 1 B atom in the vicinity. Si corresponds to undercoordinated oxygen, i.e. non-bridging oxygen (NBO) atom, atom with 1 Si atom.) Table 4 presents all variables used in Eq. (4). MD simulations easily enable the counting of these types of variables via a cut-off.

For glass former (Si or B) to be bonded to an O atom, it must lie within a cut-off radius of 2.1 Å and 2.0 Å for Si and B atoms respectively. Loose O atoms (i.e. an O atom not connected to any former) do not occur. Only, a small number of three coordinated O atoms arise in some glassy compositions. Yet, the definition of $D_{\text{total}}$ includes them. If $D_{\text{total}} = 1$, then the glass is fully polymerized (i.e. all O atoms are bonded to 2 or more network formers). If $D_{\text{total}} < 1$, then the glass has some depolymerization (i.e. the smaller is $D_{\text{total}}$, the more depolymerized the glass is). Similarly to Eq. (4) the contribution to the degree of polymerization for each network former is:

$$D_{\text{Si}} = \frac{2 \text{SiSi} + 1 \text{SiB} + 3 \text{SiSiB} + 2 \text{SiSiB} + 1 \text{SiB}}{\text{Si} + 8 + 2 \text{SiSi} + 2 \text{SiB} + 2 \text{SiSi} + 3 \text{SiSiSi} + 3 \text{SiSiB} + 3 \text{SiSiB} + 3 \text{SiB}}$$  (5)

for the silica units and

$$D_{\text{B}} = \frac{1 \text{SiB} + 2 \text{BB} + 1 \text{SiSiB} + 2 \text{SiBB} + 3 \text{BBB}}{\text{Si} + 8 + 2 \text{SiSi} + 2 \text{SiB} + 2 \text{BB} + 3 \text{SiSiSi} + 3 \text{SiSiB} + 3 \text{SiSiB} + 3 \text{SiBB} + 3 \text{BBB}}$$  (6)

for the boron units.

Data shown in Fig. 9 originates from fracture simulations on SBN systems [42]. These simulations invoked the same potentials as described above. Fracture simulation details can be found in reference [47].

3. Results

3.1. SCC behavior as a function of chemical composition

Fig. 3 depicts the curves $v$ vs. $K_v$ characteristic of the SCC response for the glass composition under consideration herein for constant $K_{\text{SN}}$: (a) $K_{\text{SN}} = 2.5$ and (b) $K_{\text{SN}} = 4.5$. The axes are semi-logarithmic. The curves exhibit the shape expected from literature [1, 4], with a sharp jump of $v$ at the environmental limit $K_v$ (region 0) followed by an exponential increase of $v$ with $K_v$ (region I). Variations occur with the glass’s chemical composition. The amount of [Na$_2$O] drives these changes.

3.1.1. Region 0

First, the SCC curves shift to higher $K_v$ values as [Na$_2$O] increases (see Fig. 4 and Table 1). Note that neither SBN59 nor SBN63 display a clear observable threshold. Applying lower $K_v$ values to both glasses did not produce a measurable variation in the length of the crack tip. For the other glasses with a clear observable threshold, $K_v$ increases roughly linearly with the amount of sodium in the system. This means that in general a SBN
The role played by alkali content on the value of $\beta$ is highlighted in the literature. Section 4.1 provides a discussion of the various mechanisms proposed to explain this observation.

### 3.1.2. Region I

The slope of the $v$ vs. $K$ curve in region I steepens as Na$_2$O increases. The curve in this region I is classically modeled either by Wiederhorn's exponential law derived from the reaction-rate theory [1,4,48,49]:

$$v = v_0 \exp (\beta' K)$$

or by Maugis power law:

$$v = v_0 (K/K_0)^n$$

Within these two frameworks, $\beta' = d(\log v)/dK$ and $n = d(\log v)/d(\log K)$ defines the steepness of the SCC curves. Table 1 presents results on $\beta'$ and $n$ computed for the 7 SBN glasses herein. Fig. 5 presents their evolution with [Na$_2$O]. Initially, the amount of sodium does not significantly alter the slope; however, as [Na$_2$O] increases above 20% the slope drastically increases. This means that the corrosion speed once SCC is triggered (i.e. when $K > K_0$) increases as [Na$_2$O] increases: A step of 0.02 MPa/√m in $K_0$ implies an increase in the velocity of ~150% for SBN12 ([Na$_2$O] = 12.2%) and ~550% for the SBN35 ([Na$_2$O] = 30%). Literature does document the role of the chemical composition on $K_0$; on the other hand, the role of the glass's chemical composition on the slopes $\beta'$ and $n$ remains virtually undocumented.

### 3.2. Effect of chemical composition on the relative proportion of chemical bonds, in contrast with that on SCC

Since the pioneering work of Charles and Hillig's [50], the $v$ vs. $K$ curve in region I is usually modeled via the chemical reaction rate theory [1,48–50], which explains the exponential dependency of $v$ with $K$. In this framework, the nature and proportion of chemical bonds encountered in the corroding glass selects $v$. Furthermore, many researchers cite the Si–O–Si bond to be the limiting factor in the propagation of the crack front [51–54]. If this is true, then there should be a clear dependency on the number of bonds versus the slope in Region I. As stated in Section 2.5, MD simulations enable the counting of the number of bonds in the SBN systems. Counting, comparing and contrasting these variables to $\beta'$ and $n$ aids in confirming or refuting the long standing hypothesis that the Si–O–Si bond controls the crack propagation.

Fig. 6 depicts the normal coordinated bridging oxygen atoms of different nature and $\beta'$. These figures reveal the lack of generic trends. Similar results occur for $n$. The nature and relative proportion of chemical bonds formed by bridging oxygen atoms in the SBN glasses are not the key parameters responsible for selecting the SCC behavior in region I.

A few over coordinated oxygen atoms (i.e. oxygen atoms with 3 network formers in their vicinity) exist in the systems. However, they are extremely rare (<2% total, i.e. considering all of the O atoms in the glasses, in low sodium glasses and <1% in high sodium glasses). No correlation exists between the number of over coordinated oxygen atoms and the slope in region I.

Moving to a more mesoscale parameter, $D_{Si}$ and $D_{B}$ reveal the partial glass depolymerization for the Silica and Borate units, respectively. Fig. 7 depicts these results with $\beta'$. Similar figures exist when considering $n$. When separating the two $K_{SBN}$ values, $\beta'$ increases somewhat with depolymerization.
On the other hand, considering the glass as a whole and calculating $DPT_{\text{Total}}$ reveals a clear trend. Moreover, there is a collapse of the data for the two different $K_{\text{BON}}$ values. Increasing the polymerization of the glass decreases $\beta_c$ until $DPT_{\text{Total}} \approx 0.91$ afterwards $\beta_c$ is constant within the error of the data. Similar trends exist when looking at the variation of $n$ with $DPT_{\text{Total}}$.

Another way to catalog the degree of depolymerization in the glasses is by the number of non-bridging oxygens (NBO). Fig. 8 reveals $\beta_c$ dependency on the total number of NBO atoms in the system. A clear trend exists, similar trends exist when considering $n$. Initially, $\beta_c$ is independent of the number of NBOs up until about 17%. Afterwards, $\beta_c$ increases drastically with the number of NBOs in the glass. Herein both the total number of NBOs and $DPT_{\text{Total}}$ are measures of the degree of depolymerization of the glass network. Both variables lead to a similar conclusion that the degree of depolymerization is the relevant structure parameter responsible for the selection of SCC behavior (characterized by the slopes $\beta_c$ and $n$).

3.3. Bonds broken in the wake of the crack front

Furthermore, MD simulations enable scientists to count the number of Si–O and B–O bonds broken by a crack front. MD simulation performed on SBN glasses (with chemical compositions similar to the ones used herein) found the number of B–O and Si–O bonds broken (for constant $K_{\text{BON}}$) to decrease with increasing sodium content [Fig. 9] [42,47]. Albite 2-D, simulations of similar glasses do reveal potential crack paths which never have to break =Si–O–Si= bonds. Thus, the probability to break a =Si–O–Si= decreases with increasing [Na$_2$O] content. Hence, in this series of glasses, breaking of the =Si–O–Si= bond should not be the limiting factor.

3.4. Effect of chemical composition on the glass network, in correlation with that on SCC

Several papers [6,12,13,15] detail how [Na$_2$O] modifies the [SiO$_2$]-[B$_2$O$_3$] network. Initially, small amounts of [Na$_2$O] transforms planar $^{13}$B units into $^{14}$B for $K_{\text{BON}} \cdot R_{\text{max}} = 0.5 + \frac{\text{Na}_2\text{O}}{\text{SiO}_2}$. Subsequently, the sodium attacks the Silica network adding non-bridging oxygen atoms (NBO) to Silica tetrahedrons for $K_{\text{BON}} \cdot R_{\text{Si}} = 0.5 + 0.25 \times K_{\text{BON}}$. For $K_{\text{BON}} > R_{\text{Si}}$, sodium attacks both the silica and boron network by forming NBO on silica tetrahedrons and transforming $^{14}$B units back into planar $^{13}$B units with one or more NBO. Table 2 presents the fractional quantities of these elementary units calculated from Barlet et al. [6]. Raman and NMR analysis enable researchers to gain additional insight into the glass structure along with confirming and extending the insights provided by MD simulations. Fig. 10 presents Raman spectra for the two different $K_{\text{BON}}$ series. Clearly, the chemical composition (along with the increasing Na$_2$O concentration) alters the Raman response of the glasses: (1) a shift of the main Si–O–Si band at 430 cm$^{-1}$ towards higher frequencies; (2) a reduction in borate-ring and borosilicate-ring features between 550–850 cm$^{-1}$; (3) a change in the $Q_n$ contribution around 900–1200 cm$^{-1}$; and (4) an increase in the B–O$^-$ peak at 1450 cm$^{-1}$. Literature links these effects to several scenarios: (1) an increase in the NBOs on the silica tetrahedral [25]; (2) an increase in the depolymerization degree predicted by Yun, Dell and Bray model [12,55,56]; and (3) an increase in the mixing of the silica and borate networks evidenced by the

Fig. 7. The figure depicts the slope versus the index of depolymerization as defined by Eq. (5) (a) and Eq. (6) (b) for the silica and borate units, respectively.

Fig. 8. (a) The figure depicts $\beta_c$ versus the index of depolymerization for the whole glass as defined by Eq. (4). The line corresponds to a power law fit: $\beta_c = 0.1 \times (DPT_{\text{Total}})^{-36} + 47$, but it is predominantly for aiding the eye. (b) The figure depicts $\beta_c$ versus the percentage of NBOs calculated from MD simulations.
increase in the danburite peak (633 cm\(^{-1}\) band) and decrease in the borate rings [26]. Another scenario evidenced in literature, but less likely due to the [Na\(_2\)O], is a decrease in the silica ring sizes associated with a shift in the 430 cm\(^{-1}\) band to higher frequencies [25,27–29].

\(\beta\) MAS NMR studies provide estimates for the number of NBO atoms in these glasses [7]. Fig. 11 displays the variation of the NBO atoms calculated from Barlet et al. [7] with respect to [Na\(_2\)O]. Comparing and contrasting these results with Barlet et al. [6] gives several interesting conclusions about the local glass structure. Sodium in both SBN12 ([Na\(_2\)O] = 12.2%), and SBN70 ([Na\(_2\)O] = 14.2%) act as network compensators on the borate network and as modifiers on the silicate network. The number of NBO atoms increases with [Na\(_2\)O] (roughly linearly, Fig. 11) and \(\beta\) (or \(n\)) increases significantly (see Fig. 8b).

### 3.5. Poisson ratio an indicator of the sodium content but not of the SCC behavior

The Poisson ratio, \(\nu\), is a continuum-level scale mechanical parameter, which embeds into itself information concerning the depolymerization of the glassy network, NBO atoms... [57]. Furthermore, Barlet et al. [7] showed that \(\nu\) was the main parameter driving the response of SBN glass under indentation. Along these lines, a natural comparison would be to compare \(\nu\) with that of the SCC behavior in region I.

Fig. 12 depicts the evolution of \(\nu\) with [Na\(_2\)O] [7]. As reported in [7], \(\nu\) is roughly proportional to [Na\(_2\)O]. Fig. 13 depicts the \(\beta\) versus \(\nu\). When sodium acts predominantly as a modifier (typically \(R_{\text{max}}\beta R_{\text{max}} = 0.5 + 0.25K_{\text{Si}}\), as in the case of SBN12 and SBN70, \(\beta\) is rather constant with \(\nu\). Afterwards, the sodium begins to act as a charge compensator on the silicate network or on the silicate and borate network. At this transition, \(\beta\) increases drastically with \(\nu\). This demonstrates that SCC in region I depends not on how much [Na\(_2\)O] is in the sample, but also on the role of sodium (modifier or charge compensator) in the glass. Thus, only considering \(\nu\) (or [Na\(_2\)O]) at the continuum scale does not easily exemplify a glass’s SCC response in region I.

### 4. Discussion

#### 4.1. Region 0 — origins of the environmental shift with sodium oxide

Region 0, or the environmental limit (\(K_e\)), displays a minimal stress required for a crack front to propagate. Not all glasses have an environmental limit, e.g. pure silica. For materials with non-existing regions 0, no

### Table 3

The table presents the target molar percentages corresponding to the values used for MD simulations. The quantity of each atomic species is specified.

<table>
<thead>
<tr>
<th>Glass</th>
<th>SiO(_2)</th>
<th>Na(_2)O</th>
<th>B(_2)O(_3)</th>
<th>Si</th>
<th>Na</th>
<th>B</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBN12</td>
<td>59.6%</td>
<td>12.2%</td>
<td>28.2%</td>
<td>251</td>
<td>103</td>
<td>237</td>
<td>909</td>
</tr>
<tr>
<td>SBN30</td>
<td>47.4%</td>
<td>30.2%</td>
<td>22.4%</td>
<td>206</td>
<td>263</td>
<td>195</td>
<td>836</td>
</tr>
<tr>
<td>SBN35</td>
<td>44.1%</td>
<td>35.45%</td>
<td>20.45%</td>
<td>194</td>
<td>312</td>
<td>180</td>
<td>814</td>
</tr>
<tr>
<td>SBN70</td>
<td>67.7%</td>
<td>14.1%</td>
<td>18.2%</td>
<td>302</td>
<td>126</td>
<td>162</td>
<td>910</td>
</tr>
<tr>
<td>SBN59</td>
<td>59.1%</td>
<td>25.0%</td>
<td>15.9%</td>
<td>267</td>
<td>226</td>
<td>144</td>
<td>863</td>
</tr>
<tr>
<td>SBN55</td>
<td>55.2%</td>
<td>30.0%</td>
<td>14.8%</td>
<td>251</td>
<td>273</td>
<td>135</td>
<td>841</td>
</tr>
</tbody>
</table>

Slightly increase, \(\beta\) (or \(n\)) decrease slightly but remain constant within a 95% (2.5 \(\sigma\), where \(\sigma\) is the width of the distribution presented in Table 1) confidence error. It is well noted that only one sample herein truly show signs of being in this region, SBN63. Thus, more extensive studies are required to understand glasses in this region.

- For SBN glasses with large enough amounts of [Na\(_2\)O] (typically \(R_{\text{max}}\beta R_{\text{max}} = 0.5 + 0.25K_{\text{Si}}\)), Na\(^+\) ions mainly act as network modifiers on the silica and borate network. The number of NBO atoms increases with [Na\(_2\)O] (or \(n\)), which embeds into itself information concerning the depolymerization of the glassy network, NBO atoms... [57]. Furthermore, Barlet et al. [7] showed that \(\nu\) was the main parameter driving the response of SBN glass under indentation. Along these lines, a natural comparison would be to compare \(\nu\) with that of the SCC behavior in region I.
matter how small the stress at the crack tip, the crack will always propagate. On the other hand, glasses with alkali atoms do exhibit an environmental limit \([3,4,58]\), as in the case herein. Lawn links the delayed onsets of crack propagation to a shielding zone which encompasses the crack tip \([59]\). Thus, the physical properties of the glass and crack front within this shielding zone (or process zone, PZ) dictate the response. There are several mechanisms behind the \(K_c\) shift hypothesized in literature:

- Enhanced diffusion of alkali atoms due to stresses which provide the energy necessary for alkali atoms to migrate out of the PZ to the crack tip or free surfaces of the sample \([54]\).
- Hydronium-\(Na^+\) exchange causing a compression in the PZ due to the larger size of the hydronium ions \([58,60,61]\).
- Blunting of the crack tip \([58]\).
- Build-up of a leaching layer which prevents water from attacking the glass network \([58]\).
- Variations in the pH at the crack tip \([58,62–64]\).

All of these mechanisms suggest that \(K_c\) should increase as \([Na_2O]\) increases for approximately constant \(K_{SNB}\). As such, they are consistent with our measurements (see Fig. 4).

Although the mechanisms suggested in literature are feasible, contemplating the model SBN glasses herein uncover possible novel scenarios. Increasing \([Na_2O]\) leads to an increase in NBO atoms on the silica network and eventually the return of planar \([SiB]\) units but with NBO atoms. This aids in shifting \(K_c\) to higher stress intensity factors. Kieu et al. \([65]\) shows that the planar \([3B]\) units can accommodate stresses by reorienting themselves due to an increase in their degrees of freedom. One can also conjecture that NBO on \([3B]\) units further increases the degrees of freedom on these units due to the decrease in polymerization of the glass.

Rountree et al. \([66]\) showed that mechanical loading of pure silica can endow the structure with an orientational order. Furthermore, Smedskjaer et al. \([67]\) attribute floppy modes in \(SiO_2-Na_2O\) glasses with NBO atoms on silica tetrahedrons \([68–72]\). Thus, one can conjecture that NBO on \([SiB]\) units has several effects: (1) increases the degrees of freedom on \([3B]\) units; (2) decreases the polymerization of the glass; and (3) increases the plasticity of the glass. These effects would aid in shifting \(K_c\) to higher values.

Literature exemplifies the formation of preferential paths/channels/pockets for glasses enriched in sodium \([65,73,74]\). It is well known that the process zone \([59]\) along with the shape of the crack tip \([75]\) aid in diffusing stresses. It is conjectured herein that the formation of preferential paths/channels/pockets, which enable the diffusion of \(Na^+\) ions, act as stress sinks (i.e. they diffuse stresses at the crack tip), and thus delay the onset of crack propagation.

Another scenario arises from the increase in the glass plasticity due to \(Na^+\) ions acting as network modifiers (rather than compensators). It is interesting to recall Grandjean et al. \([76]\) studies show that the diffusion coefficient of \(Na^+\) as a modifier is larger than the diffusion coefficient of \(Na^+\) as a charge compensator. Invoking micro-indentation tests on these glasses revealed a shift in mechanical processes from densification to isochoric shear flow as \([Na_2O]\) increases \([10,77,78]\). Rouxel and co-workers link these changes to the glass Poisson ratio which is linked to the packing fraction and depolymerization of the glasses \([77,78]\).

It is worth noting again that this set of experiments only reveals possible processes within the process zone, it is unable to discriminate the dominant effect. Further studies are needed to isolate and possibly quantify the dominant effects.

### 4.2. Region I — dependence of the slope on one particular bond in the glass

For \(K_{SNB}\) approximately constant, \(\beta\) (and \(n\)) increases with increasing \([Na_2O]\) concentration (Fig. 5). In the 1960s and early 1970s, many papers state that crack front propagation occurs via heterogeneous chemical reactions occurring at the crack tip \([1,50]\). Glaster et al. \([79]\) (which was restated by Wiederhorn in reference \([1]\)) summarized the reactions occurring on a surface via 5 successive steps (taken from reference \([1]\)):

- “Movement of the gas reactant to the surface”
- “Surface adsorption of the gasses”
- “Reaction of the surface with the gas”
- “Desorption of the products on the surface”
- “Transferring the freed product from the surface into the process zone.”

The limiting factor of the reaction is the slowest, and this slowest reaction is the one defining the velocity of the crack front. In such a scenario, the rupture of the Si–O bond is expected to be the limiting factor \([80]\). Hence, there should be a clear dependence on the number of bonds versus the slope in region I. Our analysis refutes this scenario.
since no correlation occurs between the SCC curve in region I (parameters \( \beta_1 \) and \( n \)) and the relative proportion of chemical bonds formed by bridging oxygen (Fig. 6). Furthermore, the depolymerization of just the silica or borate units fails to reveal a trend (Fig. 7). Yet, the depolymerization of the full network reveals a clear trend after an initial threshold value (Fig. 8a). This shows that the mesoscale should be considered rather than just one type of bond.

4.3. Region I and the reaction rate theory

From the reaction rate theory, Wiederhorn et al. proposed to link the slope in region I to an activation volume \( \Delta V^* \) [49,62]. From [48,49], \( \beta_1 \) is proportional to the activation volume, \( \Delta V^* \) and inversely proportional to \( \sqrt{\rho_n} \) (where \( \rho_n \) is the crack tip radius). Inverse proportionality of \( \sqrt{\rho_n} \) with \( \beta_1 \) implies that the slope increases while the crack tip radius gets smaller. Yet, as the sodium content increases the crack tip blunts more [81] or shows no variation [82]. These two ideas are inconsistent with our data. Turning to \( \Delta V^* \), \( \Delta V^* \) represents a variation in volume between the activated complex (with water molecule) and the unreacted state. In general, the Young modulus varies from 72 to 82 GPa and the Poisson ratio from 0.21 to 0.26. The change is too slight to expect such a huge increase in \( \beta_1 \). Thus, the reaction rate theory cannot explain the increase in \( \beta_1 \) in SBN glasses.

4.4. Region I and SCC driven by water diffusion

Tomozawa concluded that the diffusion of water into the crack tip aids sub-critical crack propagation. Moreover, this decreases the toughness and permits crack propagation [83]. Fig. 5a and b depicts \( \beta_1 \) and \( n \) with [Na\(_2\)O]. Increasing [Na\(_2\)O] the crack front increasingly encounters NBO atoms with sodium (i.e. sodium acts as a network modifier) charge compensation type bonds (i.e. \( \equiv(Si \text{ or } B)\cdot\equivNa\cdot\equivO \)), where \( \equiv \) is the glass network [65]. Hence, increasing [Na\(_2\)O] favors water penetration and increases the slope. Celarie [84] specifically observed migration of sodium ions towards the free surface during crack tip propagation. The occurrence of this mechanism preferentially opens these weak paths aiding in the penetration of water, per Tomozawa’s theory. Finally, Tomozawa found an increased resistance of the glass to SCC which he attributes to an enhanced plastic flow at the crack tip [85]. It is true that plastic flow at the crack tip will shift \( K_c \) to higher \( K_c \) values, but if it deters the velocity in SBN glasses, then the slope should be lower. Herein, it is higher.

The interpretation of the slope in the region I cannot be rationalized via the Wiederhorn’s model. Tomozawa’s theory maybe consistent with the huge variation in slope as a function of the sodium content. On the other hand, if the slope were impacted by plastic flow processes in this series of glasses, the slope should decrease rather it increases. The penetration of water molecules sets up a preferential weak path along sodium rich regions (and their corresponding NBO atoms). Moreover, the increase in [Na\(_2\)O] increases the glasses reactivity with water. This in turn forms a weaker glass and due to the depolymerization of the glass the slope increases.

4.5. Region I and the glass structure

The SBN glass structure changes drastically with the amount of [Na\(_2\)O] as discussed above (see Raman images Fig. 10). An interesting region I SCC phenomenon occurs when you consider the sodium role as a network compensator or a network modifier.

When sodium is predominantly acting as a network compensator on the boron network (i.e. SBN12 and SBN70), few NBO atoms exist in the glasses (Fig. 11). Thus, the glasses remain rather connected (DP around 1) and the slopes are rather similar (Fig. 8a).

When sodium predominantly acts as a network compensator on the boron network and a network modifier on the silica network (SBN63), a relatively small number of NBO atoms exist (Fig. 11). The example herein, SBN12, has a slight decrease in the slope. This glass is highly connected with the greatest number of [\text{^14B}] units, but has about 25% of the silica tetrahedrons with NBOs. The [\text{^14B}] units affect the rigidity of network and decrease the floppiness of the NBO atoms, and the overall effect causes a slight decrease in the slope.

For the rest of the samples, the slope increases significantly with the amount of sodium. Sodium acts as a network modifier for both the Boron and Silica network in these samples. This causes depolymerization in samples and increases the “floppy modes” available to the glasses, allowing as seen above for the \( K_c \) to increase. However, due to the preferential paths (channels/pockets) setup by the Sodium atoms \( H^+ / H_2O / H_3O^+ \) is able to penetrate easier into the process zone, thus causing weak points. The fractures in these samples are not really the propagation of the crack front, but the merger of weak points in the glass. This idea is further enhanced by Fig. 9 which shows the number of Si–O and B–O bonds broken as the crack propagates to decrease significantly as [Na\(_2\)O] increases. In other words, if the bonds are not in the wake of the crack, the crack front will not break them.

5. Conclusion

In summary, the work herein demonstrates that [Na\(_2\)O] plays an important role on region 0 and I for the 7 Ternary SBN glasses examined herein. Increasing [Na\(_2\)O] shifts \( K_c \) to higher values. Region I provided an unexpected and unexplored response of the glass as a function of [Na\(_2\)O] role in the glass. Increasing [Na\(_2\)O] has a profound effect on the steepness of the SCC curve as the stress intensity factor increases. This effect is highly nonlinear: For \( K_{SBN} < K_{f1} = 0.5 + 0.25K_{SBN} \) (which for
the glasses considered herein corresponds to [Na₂O] ≤ 20%, a slight decreasing trend is barely visible, but within the uncertainty, these values are constant. To understand if this is a true trend or just the spread of the data, a larger selection of samples are needed within this zone. On the other hand when \( R_{\text{SH}} = R_{\text{R}} = 0.5 + 0.25 R_{\text{SH}} \) (which for the glasses considered herein corresponds to [Na₂O] ≤ 20%), the logarithmic slope \( \beta = d(\log V)/d(\log k) \) dramatically increases with [Na₂O]. This cannot be understood by looking at the relative proportion of bonds. Rather the mesoscale (interconnects, rigidity, arrangement non-interconnected oxygen atoms, and structure of the glass) dominates the behavior, and sodium’s role as a network modifier (too both the silica and borate units) is of utmost importance on this mesoscale structure (its degree of depolymerisation) and subsequently on the selection of the SCC behavior. Quite surprisingly, the Poisson ratio \( \nu \) fails to fully track this role. These series of findings should stimulate scientific investigations of the full Ternary diagram. Understanding the full Ternary diagram will aid in developing the best glass for specific uses.

Acknowledgments


Fig. 13. The evolution of \( \beta \) (using Wiederhorn’s model [1,48,49]) with the Poisson ratio \( \nu \).

Appendix A. Estimate of humidity and temperature during SCC experiments

Table A1

<table>
<thead>
<tr>
<th>Glass</th>
<th>T (°C)</th>
<th>RH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBN12</td>
<td>28(±3)</td>
<td>45(±7)</td>
</tr>
<tr>
<td>SBN30</td>
<td>31(±4)</td>
<td>41(±2)</td>
</tr>
<tr>
<td>SBN35</td>
<td>34(±3)</td>
<td>46(±5)</td>
</tr>
<tr>
<td>SBN70</td>
<td>30(±4)</td>
<td>43(±3)</td>
</tr>
<tr>
<td>SBN63</td>
<td>28(±3)</td>
<td>43(±3)</td>
</tr>
<tr>
<td>SBN59</td>
<td>28(±3)</td>
<td>43(±3)</td>
</tr>
<tr>
<td>SBN55</td>
<td>27(±3)</td>
<td>45(±5)</td>
</tr>
</tbody>
</table>

*Corresponds to the average temperatures and RH recorded by the experimenter during the SCC experiments.

Corresponds to average seasonal measurements as the experiments progressed continuously.


